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The Royal Society of Chemistry

Cite this: DOI: 10.1039/c0xx00000x

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PAPER

One-step method to produce methyl-D-glucoside from lignocellulosic biomass

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

One-pot acid-catalyzed methanolysis was applied to the liquefaction of biomass to obtain high molar yield of methyl-D-glucoside at moderate temperature in a short time. A high bamboo conversion ratio (85 wt%) of bamboo and high molar yield of methyl-D-glucoside (40.6 mol%) were achieved. The conditions for high yield were methanol/bamboo mass ratio of 7 (350 mL methanol and 40 g bamboo), 2.0 wt% of catalyst, reaction temperature of 200 °C and reaction time of 10 min. Both hemicelluloses and cellulose (holocellulose) in the lignocellulosic biomass can convert into methyl-D-glucoside, a key and stable product. Methanolysis of biomass proved more efficient than its hydrolysis with an acid catalyst under similar reaction conditions, in water lowered glucose yields to only 2–8 mol%.

Key word: lignocellulosic biomass; methyl-D-glucoside; liquefaction

1. Introduction

Conversion of lignocellulosic biomass to obtain valuable chemicals is of global interest due to the decreasing supply of petroleum.[1–3] In recent years, a great deal of efforts has been directed at developing a simple and effective process to produce high added-value chemicals from lignocellulosic biomass.[4–7] Many studies have attempted to produce monosaccharide by hydrolysis of cellulose and hemicelluloses,[8] which are the main carbohydrate components of lignocellulosic biomass. The produced monosaccharide was then transformed to 5-hydroxymethyl furfural (HMF),[9] sorbitol,[10] gluconic acid,[11] and alkyl-glucosides.[12] However, the glucose sugars formed in water by the degradation of cellulose are too active to exist in stable forms.[13] Methyl-D-glucoside (MLG) (include methyl-α-glucoside and methyl-β-glucoside) formed in methanol was more stable than the products (glucoses) formed in water,[14] and methanolysis of biomass is more efficient than its hydrolysis.[15–17] As a green and environment-friendly process, the conversion of cellulose into high added-value chemical such as MLG, has attracted more attention for extensive research.[18]

Many solvents[16,19] and catalysts[20–23] have been used in producing chemicals from cellulose. Alcohols as solvents have received increasing attention for alcohols can suppress humins formation[24] and can be used in one-pot reactions.[25,26] Deng[19] proposed an effective method of converting microcrystalline cellulose to methyl glucoside using a sulfonated carbon-based catalyst. Although different solvents and catalysts can convert cellulose into chemicals with a high yield, the low purity and selectivity due to the further degradation of product in harsh conditions, should be improved.[27] Beyond that, many morphological and structural differences between cellulose and lignocellulosic biomass add difficulties of producing chemicals.[28] The change from the model compound (cellulose) to what is encountered in real lignocellulosic biomass, requires appropriate modifications to the conversion process so that the liquefied products can be fractionated easily to obtain the desired fractions for further refining.

In China, moso bamboo (*Phyllostachys edulis*) is the most important bamboo species and commands large areas in south of China. About 15×10^8 poles of moso bamboo are available annually in China. The moso bamboo with a fast growth time, high output yield and widely use, has been studied as a raw materials for industrial product for a long time. However, large amounts of bamboo (accounting for 30%–40% of the whole bamboo) are not fully utilized when it is converted into useful products such as furniture. Ideally, this industrial lignocellulosic bamboo waste should be utilized to obtain high-value products, and its liquefaction using organic solvents is a particularly important part of the thermo-chemical conversion process that leads to high-value products.

The research reported in this paper sought to produce MLG (include methyl-α-glucoside and methyl-β-glucoside) using one-step and direct liquefaction of moso bamboo in methanol with low concentration of an acid catalyst. Molar yields of MLG obtained under different reaction conditions were compared. At the same time, the processing decolorization and purification of MLG was also investigated to preparing pure MLG crystals.

2. Experimental

2.1 Chemicals

MLG, 5-methoxymethyl furfural (MMF), and methyl levulinate (MLA) used for calibration were obtained from Aladdin company (≧99% pure). All other chemicals in the study were of analytical grade, commercially available, and used without further purification. The moso bamboo used in the experiments was collected from a local farm (Sichuan, China) as industrial waste bamboo. Its composition (w/w) was measured, the results were as follows: cellulose (hexose), 46.2 wt%; pentosan (pentose), 23.7 wt%; lignin, 25.1 wt%; ash, 1.4 wt%. The starch, cellulose, and bamboo were dried under vacuum at 105 °C for 6 h and sieved through a 40-50 mesh (size 300-425 μm) sieve.

2.2 Analysis methods

Analysis of the products (MLG, MLA and MMF) were conducted on a mass spectrometer (MS, Agilent 5975C VL MSD), and the products were separated into their components using a gas chromatograph (GC, Agilent 7890A) equipped with a fused capillary column (HP-5, L=30 m, inner diameter=0.25 mm, and film thickness=0.25 μm) with 5% phenyl methyl silox and 95% dimethylpolysiloxane as the stationary phase. Temperature programming was held at 50 °C for 2 min and then heated to 280 °C at the rate of 5° C/min, followed by 30 min at 280 °C. Injector temperature was maintained at 280 °C. The carrier gas was helium at a flow rate of 1.8 mL/min (linear velocity 45 cm/s) and 90 kPa inlet pressures was the carrier gas employed. The samples (0.2 μL) were injected neat with 1:20 split ratio at a split flow rate of 1.5 mL/min. The identification of the components of the products was confirmed using total ion chromatograms as well as a fragmentation pattern. The MS detector was operated in the electron ionization mode (70 eV) with an ionization temperature of 230 °C. The mass spectra were recorded in electron ionization mode for *m/z* 50–550. The quantitative analysis of methyl-α-glucoside (M-α-G) and methyl-β-glucoside (M-β-G) were analyzed on HPLC (Shimadzu LC–10ATVP) instrument with column Aminex HPX–87H, and RID–20A detector. The mobile phase comprised 0.005 mmol/L sulfuric acid (sonication de-aeration) in water with a flow rate of 0.6 mL/min, and the column temperature was maintained at 50 °C. Yields of both M-α-G and M-β-G were estimated using the external standard curve method. The retention times were shown in Fig. 1 as follows: M-α-G, 3.27 min; M-β-G, 3.81 min; MLA, 7.94 min; MMF, 11.59 min. The by-products (MLA and MMF) were analyzed quantitatively by gas chromatography (GC) using a flame ionization detector and their yields estimated by the internal standard curve method with *n*-octanol as the internal standard. Gas chromatography (GC) analysis of samples were performed employing a gas chromatograph (Agilent 7890A) fitted with flame ionization detector (FID), printer-plotter and an electronic integrator, using a bonded phase fused silica capillary column (HP-5, L=30 m, inner diameter=0.32 mm, and film thickness=0.25 μm). Nitrogen at a flow rate of 30 mL/min (linear velocity 27 cm/s) and 48 kPa inlet pressure was the carrier gas employed. Temperature was programmed from 50 for 2 min and then heated to 200 °C at 5 °C/min ramp rate with a final hold time of 5 min. Injector temperature was maintained at 250 °C. The samples (1 μL) were injected neat with 1:50 split ratio at a split flow rate of 1.5 mL/min. The analytical errors were in the range of ±1%. Functional groups on MLG were measured by United States NICOLET's FT–IR spectra Nicolet iS10. The test ranged from 4600 cm^{-1} to 500 cm^{-1}, with a resolution greater than 0.4 cm^{-1}, ASTM standard linearity better than 0.1% T, and wave number accuracy greater than 0.01 cm^{-1}. The ^{1}H–^{13}C correlation heteronuclear single-quantum coherence (HSQC) nuclear magnetic resonance (NMR) spectrum was recorded using a Bruker DRX 500 NMR spectrometer operating at 500 MHz. The measurements were conducted in D$_2$O at 30 °C, and tetramethylsilane (TMS) was used as an internal standard.

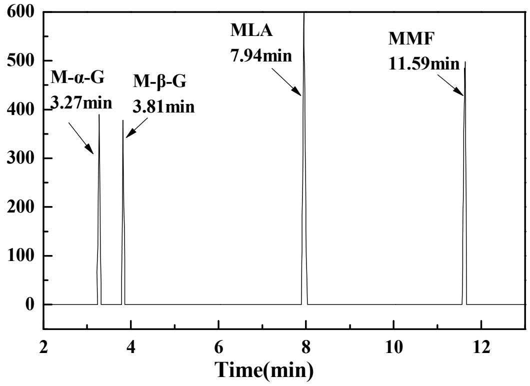


Fig. 1 The HPLC analysis of standard M-α-G, M-β-G, MLA, and MMF.

2.3 Experimental procedure

Experiments were carried out in a high-pressure autoclave fitted with a thermocouple, a stirring device, and a pressure gauge. Materials (batches of 40 g each) were introduced into a solution of acid catalyst in methanol, and the mixture was heated in an autoclave at the set temperature and stirred for a designated period of time beginning from the moment the set temperature was reached. The reaction time was the duration over which the highest constant temperature was maintained. The reaction was stopped by cooling the solution in a water bath to room temperature.

For each experiment, a solution of an acid catalyst in methanol and a given amount of bamboo (40 g) were introduced into the reactor, which was then brought to the desired temperature by external heating. The mixture was stirred at 600 rpm for liquefaction. The temperatures ranged from 140 °C to 240 °C in increments of 20 °C. The amount of acid catalyst (H_2SO_4, $C_7H_7SO_3H$, or $H_4SiW_{12}O_{40}$) was varied from 1 wt% to 4 wt% (w/w) and the initial amount of methanol from 250 mL to 450 mL. At the end of the set reaction time, the reactor was taken off the stove and cooled quickly in an ice-cold water bath to terminate the reaction. The reaction mixture was taken out from the autoclave and filtered through a membrane filter (pore size 10 μm). The filter cake (residue) was repeatedly washed with methanol to extract the residual as completely as possible. The filtrate was evaporated under vacuum at 50 °C to remove and recycle the methanol. The residue was dried at 105 °C for 5 h to estimate the amount of char.

The formulae for bamboo conversion are given below.

$$\text{Conversion (wt \%, w/w)} = \left(1 - \frac{\text{amount (weight) of solid residue}}{\text{amount (weight) of materials}}\right) \times 100\%$$

$$\text{Molar yield of MLG (mol\%)} = \frac{m(\text{MLG}) \times \text{mass yield of MLG (measured by HPLC)(wt\%)} \big/ 194\ \text{(molecular weight of MLG)}}{m(\text{material}) \times \text{cellulose content(wt\%)} \big/ 180\ \text{(molecular weight of glucose)}} \times 100\%$$

$$\text{Molar yield of MLA (mol\%)} = \frac{m(\text{MLA}) \times \text{mass yield of MLA (measured by GC)(wt\%)} \big/ 130\ \text{(molecular weight of MLA)}}{m(\text{material}) \times \text{cellulose content(wt\%)} \big/ 180\ \text{(molecular weight of glucose)}} \times 100\%$$

Table 1 Effect of different solvents on MLG [a] recrystallization.

Solvents	Recrystallization yield (wt%)	Solvent recovery yield (wt%)
methanol	60.27	95.11
petroleum ether	72.11	93.02
acetone	80.04	94.19
95 wt% ethanol	85.72	97.53

[a] Reaction conditions: 40 g starch in 150 mL methanol with 2 g toluenesulfonic acid; time, 2 h; temperature, 200 °C.

2.3.2 Recrystallization of starch liquefaction product

Glucose is commonly used for preparing alkyl-glycosides (such as MLG) to obtain high yields (90 wt%, w/w) after dehydration of alcohols using acid catalysts[29]. The most abundant and inexpensive source of glucose is starch, which consists of repeating glucose units. For the liquefaction of starch, 40 g starch was mixed with 150 mL methanol and 2 g toluenesulfonic acid and the mixture was autoclaved by raising the temperature at the rate of 3 °C/min and stirring until the set conditions (120 °C, 0.5 MPa) were reached which were maintained for 120 min. The reaction mixture was taken out from the autoclave with methanol and filtered through a membrane filter (pore size 10 μm). Raw MLG was obtained after subjecting the liquid mixture to rotary evaporation to remove the methanol. The raw MLG was recrystallized with mass fractionation using different solvents such as methanol, petroleum ether, acetone, and 95 wt% (w/w) ethanol.

2.3.3 Bleaching the cellulose liquefaction product

The product of liquefaction is a dark yet clear liquid, and bleaching it is especially important in obtaining MLG. Four bleaching agents were used: hydrogen peroxide (30 wt % H_2O_2 in H_2O), a liquid; ozone (O_3), a gas; and two solids, namely sodium bicarbonate ($NaHSO_3$) and activated carbon (a form of carbon that has been processed to make it extremely porous, which has a very large surface area for adsorption[30]). Three of the bleaching agents ($NaHSO_3$, H_2O_2, and activated carbon) (1.0 g each) were directly added to the liquefied product (50 g), whereas ozone was introduced into the liquefied product (50 g) by using an ozone generator (50 g/h). For all the bleaching reactions, the temperature was constant at 75 °C and the mixture was stirred throughout the 60 min period.

3. Results and Discussion

3.1 Conversion of corn starch into MLG

The experiment results suggested that the direct liquefaction of starch can produce MLG with low concentration acid catalyst in methanol medium. The starch can be completely converted into a liquid product, and HPLC results indicated the content of MLG with 95 wt%. Table 1 showed the recrystallized yield, is calculated by the quality of MLG crystals, 95 wt% ethanol is the best solvent for recrystallization, and the high yield of MLG crystals is 85.72 wt%. To obtain the same product MLG, the recrystallization can also be used in biomass liquefaction mixture samples to get MLG.

3.2 Conversion of cellulose into MLG

The cellulose with methanol and low concentration acid catalyst was used for liquefaction in an autoclave. When several dissolved acid catalysts (such as H_2SO_4) are used acid in methanol, cellulose is converted directly into MLG in a clean and one-pot catalytic process that gives yields of MLG amounting to more than 40 wt% of the liquefied mixture[16]. However, the dark liquid (Fig. 2) needs to be bleached before it can be processed to obtain MLG. The results of using four bleaching agents can be seen in Fig. 2.

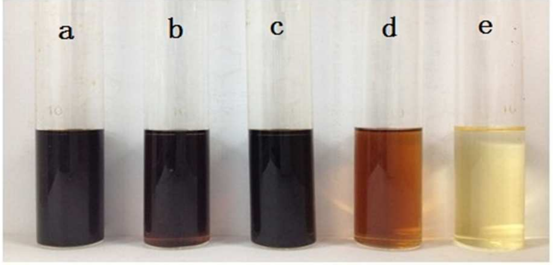


Fig. 2 Effect of different agents on liquefied product bleaching. (a) liquefied product, (b) H_2O_2, (c) $NaHSO_3$, (d) O_3, and (e) activated carbon.

3.3 Effect of various catalysts on bamboo liquefaction

Non-catalytic degradation of bamboo was also examined in our experiment, and not completely converting the bamboo into product. Several dilute mineral and organic acids including HCl, H_3PO_4, HNO_3, H_2SO_4, NH_2SO_3H, HCOOH, and $C_7H_7SO_3H$ were then evaluated as catalysts at a concentration of 2 wt%. H_2SO_4 is proved the most efficient catalyst; HCOOH and HNO_3 performed poorly; and HCl is the poorest performed catalyst in the experiment (Table 2). It is probable that the higher boiling point and stronger acidity of H_2SO_4 (lower pKa) contributed to its efficiency. Small quantities of MLA and MMF were also found in the experiment that used H_2SO_4 as catalyst, probably by subsequent conversion of MLG and hemicelluloses in the presence of the dilute acid.

Table 2 Efficiency of various acid catalysts in converting bamboo to MLG[a].

Entry	Catalysts	Conv. (wt%)	Yield[b](mol%)			
			M-α-G	M-β-G	MLA	MMF
1	Blank	0.33	0.06	0.00	0.00	0.08
2	HCl	2.02	0.26	0.70	1.79	0.98
3	HNO_3	7.45	3.93	2.64	0.08	1.54
4	H_2SO_4	82.79	30.78	8.79	4.21	2.64
5	$H_3PW_{12}O_{40}$	79.28	18.84	6.50	3.04	2.70
6	$H_4SiW_{12}O_{40}$	80.39	18.89	10.04	4.63	2.11
7	HCOOH	1.79	0.26	0.00	0.21	0.38
8	NH_2SO_3H	25.61	11.44	10.40	0.53	3.98
9	$C_7H_7SO_3H$	61.73	22.90	8.94	7.51	5.25
10	ZrO_2	35.10	10.84	6.63	0.66	0.00
11	HZSM-5	11.32	4.28	2.48	1.21	0.88

[a] Reaction conditions: catalyst 1.0 g, bamboo 40 g, methanol 350 mL, temperature 200 °C, time 20 min;

[b] M-α-G, methyl-α-glucoside; M-β-G, methyl-β-glucoside; MLA, methyl levulinate; MMF, 5-methoxymethyl furfural (MLG include M-α-G and M-β-G; yields based on HPLC and GC analysis).

The heteropolyacids such as $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were adopted as catalysts in liquefaction; the complex structure of the lignocellulosic biomass prevented them from liquefying bamboo efficiently. However, other acids, when evaluated for bamboo methanolysis, performed somewhat better: mesoporous ZrO_2 resulted in MLG yield of 17.47 mol% although. Zeolite H-ZSM-5 showed very low reactivity, possibly as its pores are too small (0.55 nm) to be effective in bamboo methanolysis.

Using H_2SO_4 at low concentrations as a catalyst is a highly promising strategy for synthesizing MLG from methanolysis of biomass: H_2SO_4 can offer enough hydrogen ions (H^+) to complete the reaction and results in negligible quantities of dimethyl-ether, an undesirable by-product of the dehydration of methanol[24]. Besides, subsequent neutralization (with NaOH) of the spent acid generated less solid waste (about 1 g), thus minimizing the environmental impact of the process.

3.4 Effects of various parameters on the methanolysis of bamboo

To understand the degradation of lignocellulosic biomass in methanol at low concentrations of the chosen catalyst, namely H_2SO_4, in order to obtain the highest possible yields of MLG, the next step was to vary the different processing parameters including the amounts of catalyst and methanol and the duration and temperature of the reaction. The effects of varying these parameters were evaluated by quantifying and analyzing the lignocellulosic biomass and the target product (MLG) as well as the main by-products, namely MMF and MLA.

On the whole, it was found that most of the biomass (more than 80 wt%) is converted within the first 20 min; the yield of MLG too is high (close to 40 mol%) during the initial stage of bamboo methanolysis but decreases gradually as the reaction proceeds. The yield of MMF and MLA is markedly lower than that of MLG, which is the subsequent conversion of MLG, needs more time or more of the catalyst. It was also found that the processing of converting bamboo into MLG is much faster and easier than the subsequent conversion of MLG to MMF and MLA in methanol.

3.4.1 Amount of catalyst

Increasing the concentration of the catalyst boosted MLG yields initially, but further increase in catalyst concentration had little effect on the yield (Table 3). The yields of MLG were 39.57 mol% with H_2SO_4, 30.48 mol% with $H_4SiW_{12}O_{40}$, and 31.84 mol% with $C_7H_7SO_3H$. The yield of MLG with 2.5 wt% H_2SO_4 was only slightly higher than that with 2 wt% H_2SO_4, which shows that excess H_2SO_4 has little effect on yield.

However, higher acid concentrations not only corrode reactor equipment but also increase the yield of by-product such as MLA, at the expense of MLG. MLA is probably formed as a result of acid-catalysed conversions of MLG from bamboo at high catalyst concentrations. Therefore, the optimum catalyst concentration for the synthesis of MLG from methanolysis of bamboo is approximately 2 wt% (per 40 g bamboo).

Table 3 Effect of catalyst amount on the conversion of bamboo to MLG. [a]

Catalyst	Catalyst amount (wt%)	Conv.(wt%)	Yield[b] (mol%)			
			M-α-G	M-β-G	MLA	MMF
H_2SO_4	1.5	73.82	12.61	6.59	5.64	0.21
	2	80.23	29.41	9.04	2.61	6.29
	2.5	82.79	30.78	8.79	4.21	2.64
	3	64.19	27.89	2.85	3.55	5.26
$C_7H_7SO_3H$	1	55.33	17.16	7.54	0.84	5.06
	2.5	61.73	22.90	8.94	7.51	5.25
	4	66.37	20.58	3.89	2.91	6.54
$H_4SiW_{12}O_{40}$	1	60.26	19.73	3.80	3.03	8.39
	2.5	80.39	18.89	10.04	4.63	2.11
	4	82.03	25.14	5.34	9.43	0.34
	6	84.31	15.87	6.35	10.21	1.70

[a] Reaction conditions: methanol, 350 mL; bamboo, 40 g; temperature, 200 °C; time, 20 min;
[b] M-α-G, methyl-α-glucoside; M-β-G, methyl-β-glucoside; MLA, methyl levulinate; MMF, 5-methoxymethyl furfural (MLG include M-α-G and M-β-G; yields based on HPLC and GC analysis).

3.4.2 Methanol amount

Methanol was chosen as it is considered a cost-effective solvent in bamboo liquefaction and can also be prepared from biomass[31]. The amount of methanol is particularly important for the conversion. The reaction was performed for 20 min. As the amount of methanol increased from 250 mL to 350 mL, the rate of conversion and the molar yield of MLG increased significantly (Table 4) but when the amount of methanol was increased further to 450 mL, MLG yield decreased markedly, indicating that either the conversion was incomplete or MLG was converted to other by-products. Many earlier studies found a similar pattern[23, 29, 32]. The amount of methanol is crucial to the decomposition of bamboo into intermediate products. Therefore, the favorable amount of methanol is 350 mL of 40 g bamboo, as demonstrated in the present experiment.

Table 4 Effect of methanol amount on the conversion of bamboo.[a]

Methanol amount (mL)	Conv. (wt%)	Yield[b] (mol%)				Methanol recovery yield, wt%
		M-α-G	M-β-G	MLA	MMF	
250	26.01	7.34	4.09	8.14	2.54	73.33
300	45.97	13.86	3.93	6.36	3.75	77.89
350	80.23	29.41	9.04	2.61	6.29	80.73
400	85.03	30.39	5.35	1.30	5.51	82.23
450	86.21	23.46	4.29	0.98	2.94	75.14

[a] Reaction conditions: catalyst, 0.8 g; bamboo, 40 g; temperature, 200 °C; time, 10 min;
[b] M-α-G, methyl-α-glucoside; M-β-G, methyl-β-glucoside; MLA, methyl levulinate; MMF, 5-methoxymethyl furfural (MLG include M-α-G and M-β-G; yields based on HPLC and GC analysis).

3.4.3 Reaction time

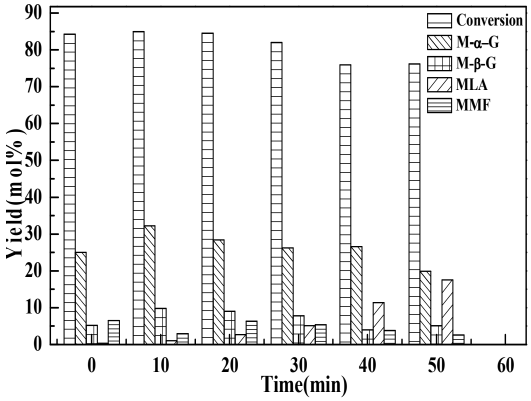


Fig. 3 Effect of reaction time on the conversion of bamboo; Reaction conditions: temperature, 200 °C; catalyst, 0.8 g; bamboo, 40 g; methanol, 350 mL. M-α-G, methyl-α-glucoside; M-β-G, methyl-β-glucoside; MLA, methyl levulinate; MMF, 5-methoxymethyl furfural (MLG include M-α-G and M-β-G; yields based on HPLC and GC analysis).

The reaction time was varied in 10 min increments from 0 min to 60 min, keeping the temperature at 200 °C and using a low concentration of H_2SO_4 (2 wt% of 40 g bamboo) as the catalyst (Fig. 3). The highest yield of MLG (40.6 mol%) was obtained in the first 10 min; with longer reaction times, the yield of MLG decreased whereas that of other by-products of degradation (such as MMF and MLA) increased, a pattern reported earlier[18]. A short reaction time of 10 min thus appears better.

3.4.4 Reaction temperature

Operating temperature is a very important parameter governing chemical reactions. In general, high temperature could contribute to the acceleration of liquefaction reaction rate and the enhancement of bamboo conversion efficiency[28]. In the present experiment, the reaction temperature was varied in 20 °C increments from 140 °C to 240 °C. As the temperature increased, so did the yield of MLG (Fig. 4) until 200 °C. At 220 °C, the yield of MLA, a by-product, was up to 15 mol%. At temperatures beyond 200 °C, MLG yield declined sharply.

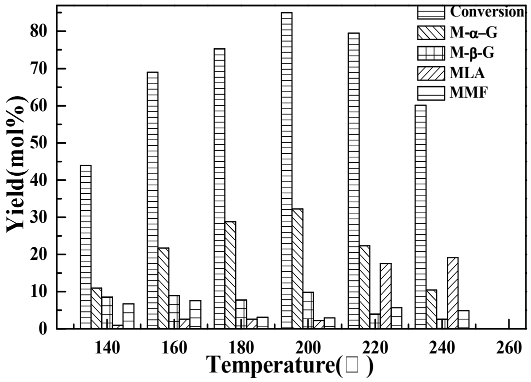


Fig. 4 Effect of reaction temperature on the conversion of bamboo.
Reaction conditions: catalyst, 0.8 g; bamboo, 40 g; methanol, 350 mL; time, 10 min. M-α-G, methyl-α-glucoside; M-β-G, methyl-β-glucoside; MLA, methyl levulinate; MMF, 5-methoxymethyl furfural (MLG include M-α-G and M-β-G; yields based on HPLC and GC analysis)

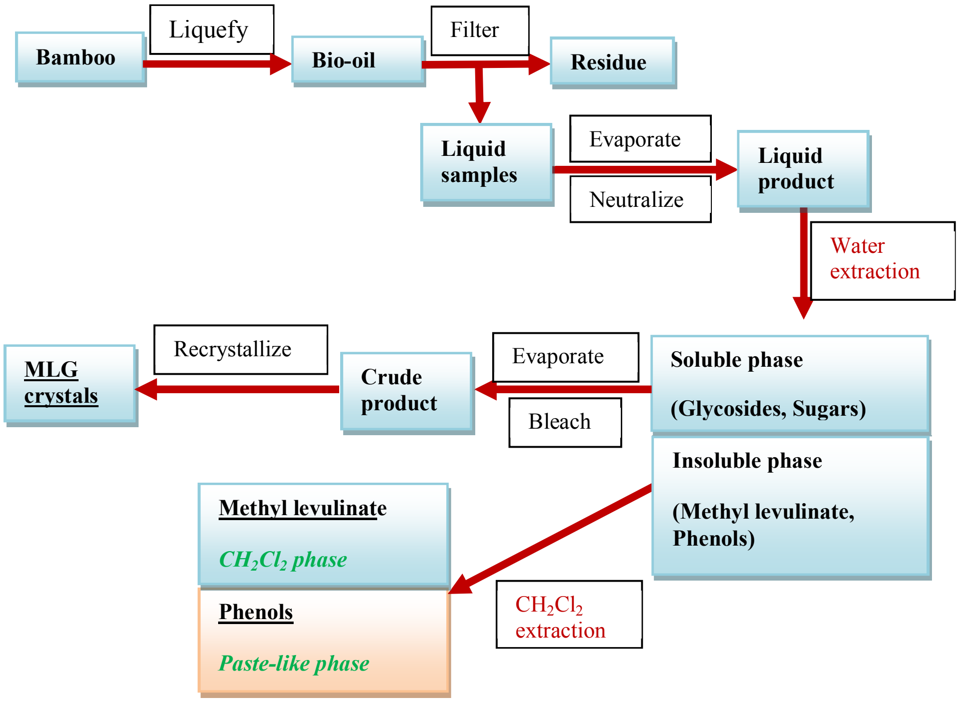
On the other hand, at lower temperatures (160 °C and 180 °C), the conversion ratio of bamboo was lower because its complex structure could not be broken down. This suggests that increasing the temperature helps in faster liquefaction of bamboo. However, it must be pointed out that at very high temperatures, MLG will be decomposed to some extent into MLA and other products of liquefaction. Generally, a moderately high temperature of 200 °C, together with a short reaction time of 10 min, low concentration of the catalyst H_2SO_4 (2.0 wt% of 40 g bamboo in 350 mL of methanol) led to high yields of MLG (40.6 mol%) and a high bamboo conversion ratio (85 wt%) of bamboo.

3.5 Purification of liquefaction product

3.5.1 Purification processing to obtain MLG

Purifying the products of bamboo liquefaction is important for obtaining pure MLG crystals. Liquefied lignocellulosic biomass product is a particularly complex substance and contains hundreds of compounds[33]. Although direct rotary evaporation is the process of choice in obtaining MLG from liquefied starch, the process does not work well with liquefied bamboo product. We therefore introduced a series of modifications such as neutralization, recovery of methanol by rotary evaporation, and water extraction (Scheme 1), which led to a pale brown but clear liquid (the soluble phase). The soluble phase was decolorized with activated carbon, after which the liquid was fully evaporated to get a crude product. The crude product was recrystallized from 95% ethanol (Fig. 5).

Fig. 5 Pictures before (a) and after (b) recrystallization of MLG product.



Scheme 1 The production and separation of MLG via the extraction from liquefied product.

3.5.2 Measurement crystal properties

The melting points of standard samples of MLG and of MLG crystals obtained in the present experiment were nearly identical, being 169–171 °C and 169.2–170.6 °C respectively (average of three runs). The two proved almost similar in other ways too: Fig. 6 shows the results of FT-IR spectroscopy (Fourier-transform infrared spectroscopy) of the standard and experimental samples, which offers strong evidence that purified MLG can be prepared from methanolysis of biomass. Additional evidence comes in the form of the absorption peak (897–906 cm^{-1}) characterized by a bending vibration β-glycoside isomers C_1-H absorption peak (Fig. 6).

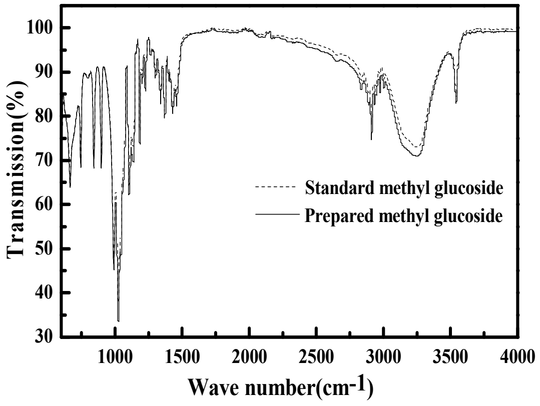


Fig. 6 FT-IR of standard MLG and experiment prepared MLG.

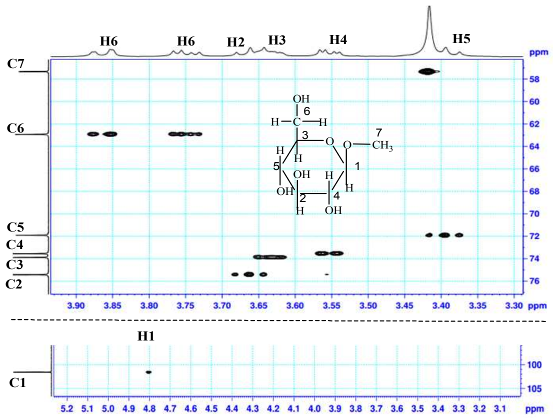


Fig. 7 The HQSC NMR of experiment prepared MLG.

Table 5 ^{13}C and ^{1}H chemical shift values (δ_C and δ_H) in NMR of experiment prepared MLG.

C NMR		H NMR	
mark C	ppm	mark H	ppm
1	101.562	1	4.800
2	75.420	6	3.853
3	73.882	6	3.750
4	73.545	7	3.665
5	71.909	2	3.640
6	62.919	3	3.550
7	57.338	5	3.416
		4	3.395

Purified samples of MLG were also subjected to HQSC NMR (Fig. 7). All these signals have similar structural features[34]; contain the same number of directly bound protons; have similar ^{13}C chemical shift values and similar $^{1}J_{C\text{–}H}$ values (Table 5).

By applying the rules for HSQC measurements, either the proton signal H3 or the ^{13}C signal cluster from C2, C3, C4, and C5 can be chosen as the secondary internal standard reference for quantifying the HSQC NMR signals originating from H2, H3, H4, and H5 in MLG crystals. All these signals share a similar structure; contain the same number of directly bound protons; and have similar ^{13}C chemical shift values and similar $^{1}J_{C\text{–}H}$ values. Signals from a small quantity of impurities present in the sample can be observed near the signal of H4 in the HSQC spectrum. The cross peaks for internal anomerics of the (1–4) linked MLG showed up at δC/ δH 101.562/ 4.820 ppm.

3.6 The conversion of bamboo in water medium

The conversion of bamboo in methanol (methanolysis) was compared with that in water (hydrolysis) under similar reaction conditions in the presence of different acid catalysts (Table 6). Hydrolysis produced glucose, xylose, and HMF but the yield of glucose was markedly lower than that of MLG obtained through methanolysis irrespective of the catalyst. Water is believed to break down hemicelluloses and release acetic acid, which continues to catalyze the reaction, producing glucose, xylose, and HMF[35]. It is likely that the products of methanolysis are significantly more stable than those of hydrolysis. Such a significant difference may lead to different end products due to the process, although bamboo is the common starting point for both hydrolysis and methanolysis. The present experiment demonstrated that methanol is a more efficient reaction medium than water for the degradation of bamboo to obtain monosaccharide. The catalytic conversion of bamboo in methanol and in water is shown in Fig. 8.

Table 6 The conversion of bamboo in methanol and water [a].

Catalyst	Catalyst amount (wt%)	In water				In methanol			
		Con. (wt%)	Yield[b] (mol%)			Conv. (wt%)	Yield[b] (mol%)		
			Glucose	Xylose	HMF		MLG	MLA	MMF
H_2SO_4	2	17.23	8.16	6.63	1.78	85.00	40.6	2.61	6.29
$C_7H_7SO_3H$	2.5	8.04	2.63	5.16	0.64	71.25	32.46	1.31	4.53
$H_4SiW_{12}O_{40}$	4	15.20	4.46	5.98	1.26	82.16	31.59	3.95	0.49

[a] Reaction conditions: water or methanol 350 mL, bamboo 40 g, temperature 200 °C, time 10 min;

[b] M-α-G, methyl-α-glucoside; M-β-G, methyl-β-glucoside; MLA, methyl levulinate; MMF, 5-methoxymethyl furfural (MLG include M-α-G and M-β-G; yields are based on HPLC and GC analysis).

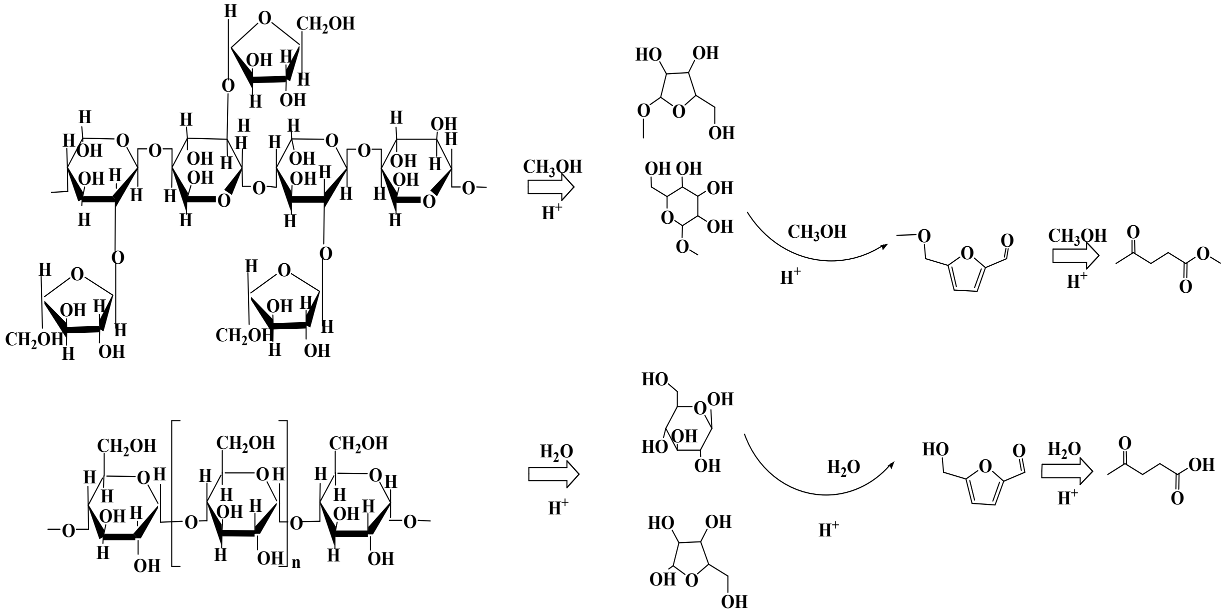


Fig. 8 Catalytic conversion of bamboo in methanol and in water medium.

4. Conclusion

The present research proposed a cost-effective and efficient process to synthesize MLG from lignocellulosic biomass catalysed by H_2SO_4 at low concentration. Different parameters with the dosage of acid catalyst concentration, methanol amount, reaction temperature and time were varied in an attempt to obtain the higher possible molar yields of MLG from bamboo. Compared with the traditional hydrolysis process, higher molar yield of MLG (40.6 mol%) was obtained by methanolysis of holocellulose from moso bamboo under moderate temperature (200 °C) in less than 10 min, which shows more efficient conversion of bamboo was much more stable products.

Acknowledgements

The authors thank the Research Institute of New Technology, and the Special Fund for Fundamental Research (CAFYBB2014ZD003). The authors also gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (31422013) for this investigation and appreciate the help given by Mrs. Li, Department of Chemical and Process Engineering, University of Canterbury, New Zealand, in modifying the manuscript.

Notes and references

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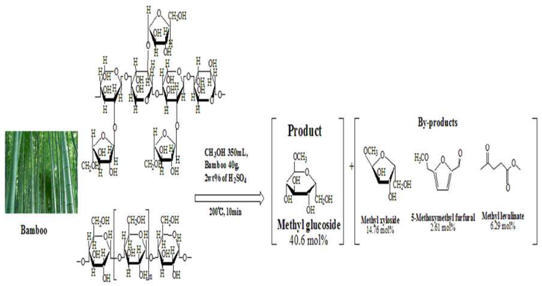
Color graphic:



Text: One-step acid-catalyzed methanolysis of bamboo biomass for the preparation of methyl-D-glucoside as high value-added chemicals.