

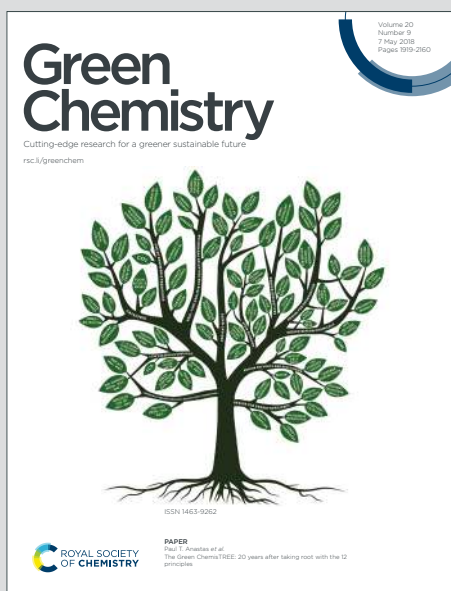
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## Directional synergistic conversion of lignocellulosic biomass with matching-solvents for added-value chemicals

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**Dimethoxymethane/methanol was creatively used as matching-solvents for one-pot synergistic converting bamboo into value-added chemicals. C6 and C5 sugars in cellulose and hemicellulose were simultaneously transformed into methyl levulinate with higher yield (48.68%). The overall reaction pathways for directional liquefaction of biomass into methyl levulinate with matching-solvent was put forward.**

Efficient use of renewable and abundant biomass can effectively reduce emission of greenhouse gas and relieve the heavy dependence of fossil fuels.<sup>1</sup> The utilization of biomass for preparing high added-value chemicals and quality fuel products could meet the demands of future energy and achieve the principle of green chemistry. In China, Moso bamboo is one of the most common lignocellulosic biomass energy crops and is planted in a large number of areas. They are widely distributed across southeast and southwest of China, approximately  $15 \times 10^8$  stems of Moso are available annually. Moso with fast growth rate, high yield and many uses, has been studied as a raw material for industrial products for a long time. However, a large amount of bamboo waste (accounting for 30–40% of the whole bamboo) is not fully utilized during the production of down-stream products, such as making furniture and paper.<sup>2</sup> Recent studies have focused on the production of high grade fuels and chemicals from the transformation of waste lignocellulosic biomass.<sup>3</sup>

Among these chemicals, levulinic acid (LA) was determined as a popular and versatile chemical derived from the conversion of carbohydrates, which can be widely applied in agriculture, pharmaceuticals, cosmetics, foods, and liquid hydrocarbon fuels or fuel additives.<sup>4</sup> Many researchers have studied the single step conversion of cellulose to industrially important LA using an acid catalyst or ionic liquids.<sup>5</sup> Nevertheless, the production of LA is limited by the cost of the separation equipment and the preparation reactor because of its high viscosity, acidity and boiling point (about 245 °C). As an alternative, methyl levulinate (MLA) has shown better performance in the preparation and separation process due to its lower boiling point (about 193 °C), non-corrosive nature, and good stability, which requires less energy consumption in the separation treatment. MLA is as useful as LA in many fields such as organic

chemistry, medicine, solvents, and cosmetics.<sup>6</sup> Besides, MLA contains short-chain fatty esters with valuable application, used as fuel additives, which can improve diesel and oil stability, flash point, non-toxicity, lubricity ability, and low-temperature fluidity.<sup>7</sup>

Some researchers have investigated the production of levulinic acid/ester from both C6 and C5 sugars or their derivatives (MCC, glucose, fructose and furfurals).<sup>8–10</sup> Hu et al studied that conversion of biomass-derived xylose, glucose, furfurals into levulinic acid/ester via a solid acidic resin catalyst with DMM/methanol.<sup>8(a),8(b)</sup> They also studied the direct conversion of furan to methyl levulinate via acid-catalysis in DMM/methanol without hydrogenation. Huang et al reported the alcoholysis of furfuryl alcohol with a Lewis acid catalyst by microwave-assistance, and the yield of MLA was 80.6% with  $\text{Al}_2(\text{SO}_4)_3$ .<sup>9</sup> Song et al investigated the conversion of MCC into MLA with an efficient catalyst  $[\text{PyPS}]_3\text{PW}_{12}\text{O}_{40}$  and the highest yields was 71.4%.<sup>10</sup> The yields of levulinates were improved in the conversion process of biomass-derived models, but the cost of raw materials has also increased.<sup>11</sup> The biomass-derived models studies were essential for determining suitable reaction conditions for transforming real biomass into high-grade levulinates.<sup>8(a),8(b),12</sup> Nevertheless, many structural and morphological differences exist among the biomass-derived models and real biomass, which has increased the complexity of producing high-quality levulinates.<sup>13</sup> In general, the directional preparation of levulinate esters/acid from the alcoholysis/hydrolysis of real lignocellulosic biomass is very meaningful and important.

Typically, levulinic esters/acids derived from biomass was produced from the alcoholysis/hydrolysis of C6 structural carbohydrates followed by the dehydration of C6 sugars via metal-containing catalysts or acid catalyst with the yields about 10%–30%.<sup>14</sup> The low yields of levulinic esters/acids from biomass have been mainly attributed to the following reasons: the polymerization of C6 sugars during the conversion of hydrolysis and dehydration process into levulinic esters/acids;<sup>15</sup> only the C6 sugars units in hemicellulose and cellulose could be transformed into levulinic esters/acids in presence of catalysis. In the hydrolysis or alcoholysis process of biomass, the C5 sugars units in hemicellulose are mainly transformed into furfurals and derivatives under the same conditions.<sup>16</sup> Furfurals can be directional converted into alkyl levulinates (fuel additives) with bifunctional catalyst (acid supported metal, such as  $\text{Pt/ZrNbPO}_4$ ) via acid-catalyzed alcoholysis reaction coupled with metal-catalyzed hydrogenation.<sup>17</sup> In the conventional method, the conversion of C5 sugars to levulinic esters/acids includes the acid-catalyzed transformation of xylose to furfural in a liquid phase, the further metal-catalyzed hydrogenated furfural into furfural alcohol,<sup>11,18</sup> and the acid-catalyzed conversion of furfural alcohol to levulinic esters/acids (Fig. S1).<sup>19</sup> The above steps include both alcoholysis reactions and hydrogenation with different catalysts and reaction conditions. Therefore, many studies concentrated on the developing of the catalytic transformation of cellulose in biomass.<sup>15,20</sup> However, the simultaneous catalytic degradation and utilization of

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carbohydrates (hemicellulose and cellulose) to produce high-quality levulinic esters/acids still remains a significant challenge.

This directional liquefaction of Moso bamboo to prepare MLA with dimethoxymethane/methanol (DMM/METH) matching-solvent is a new method that can effectively convert lignocellulosic biomass into MLA. The influence of multiple reaction parameters were studied to optimize the degradation of biomass and maximize yield of MLA under mild conditions. After the stepwise extraction and precipitation of the liquefied products under optimal reaction conditions, the absolute content of the extracted methyl levulinate was up to 88%. The DMM/METH solvents were recovered and separated with extractive distillation and could be used in subsequent experiments. The reaction pathways for the simultaneous catalytic and oriented one-pot conversion of cellulose and hemicellulose into MLA were studied in detail. The mechanisms of breaking the molecular and chemical bonds in lignocellulosic biomass with matching-solvent were put forward based on the GC-MS results. Overall, this one-pot oriented catalytic strategy is an efficient and economical design for transforming biomass into high added-value chemicals.

Table 1 shows the influence of different solvents on the conversion of bamboo and the yields of products. The transformed furans intermediates derived from monosaccharides were present in a variety of transitional forms such as furfural, 5-hydroxymethylfurfural (HMF), 5-methoxymethyl-furfural (MMF), 2-(dimethoxymethyl)-5-(methoxymethyl)-furan (DMF), 2-(dimethoxymethyl)-furan (DOF), 5-(hydroxymethyl)-2-(dimethoxymethyl)-furan (HDF). These furans are highly reactive towards any polymerization process. When methanol was used as the lone solvent, the yields of levulinates (35.68%) was relatively low. This was because only the C6 sugar substrates in cellulose and hemicellulose were transformed into MLA. This was because only the C6 sugar substrates in cellulose and hemicellulose were transformed into MLA by the intermediate compounds of 5-hydroxymethylfurfural. The C5 sugar substrates in hemicellulose were converted into furfurals rather than MLA. The differences in structure between furfural (the dehydration intermediate of C5 sugars to methyl levulinate) and 5-hydroxymethylfurfural (the dehydration intermediate of C6 sugars to methyl levulinate) is the additional hydroxymethyl group in 5-hydroxymethylfurfural. On the other hand, dimethoxymethane can be used as an electrophile to promote the transformation of furfural to 5-hydroxymethylfurfural. Pure dimethoxymethane as reaction solvent was not able to prevent the polymerization of furans. These compounds with the furan ring can react with dimethoxymethane via the electrophilic substitution reactions. However, the conversion of these compounds and the yield of levulinic acid (12.10%) were lower than the matching-solvents.

The formation of matching-solvents was combined DMM with different solvents. Under the same reaction conditions, the dissolution and chemical activity of matching-solvents were significantly different. Among the matching-solvents investigated, ethanol and methanol could significantly promote the yield of levulinic esters/acid. When DMM and METH were used as the matching-solvents, a 41.87% yield of MLA was obtained, which was higher than that from the liquefaction with ethanol and DMM (36.79%). Under other single alcohols media (e.g., 1-propanol and isopropanol), the product yields were only 31.46% and 34.27%, respectively. There are two major reasons that can contribute to these differences: 1) different dielectric properties (including dielectric loss and dielectric constant), polarity and steric effects of the different alcohols;<sup>9,21</sup> 2) different reactivity of the alcohols with different alkyl chains, which could lead to some differences in the conversion of biomass material and the yields of target products. The functional groups or molecules with high dielectric constant (dipole moments) could increase the collision frequency or average kinetic energy of the molecules. This could contribute to higher reaction rates of liquefaction. Compared with other kind of solvents (e.g.,

ethylene glycol, glycerol, and dimethyl sulfoxide (DMSO), methanol and ethanol have a relatively low boiling point. Under the same reaction temperature (200 °C), methanol and ethanol are relatively easy to reach the subcritical point, and the subcritical solvents have a relatively high reactivity. Subcritical methanol could provide a good solubility for the liquefied products and a high auto-genetic pressure for reaction system during the reaction, which could promote the transformation of biomass material to MLA. Moreover, furans as the as necessary transition intermediates for the conversion of carbohydrates (hemicellulose and cellulose) to levulinate esters, are highly reactive towards polymerization. The main reason for the low yields of levulinic esters/acid may be due to the polymerization of furfurals. Methanol as the reactant/solvent was able to completely dissolve the furans and prevent the polymerization. Matching-solvents was thus employed to tackle the polymerization of furans during liquefaction. Methanol can readily dissolve the intermediate and target products, which could promote the continuous conversion of the bamboo. With different solvents, the highest yield of levulinates (41.87%) were obtained with the matching-solvents DMM/METH.

**Table 1** Effect of various solvents on liquefaction of bamboo to MLA.

Reaction medium	Conv. (wt%)	LA yield (%)	Furans yield (%)	Glycosides yield (%)	Pressur e (MPa)	Solvent recovery yield (wt%)
Methanol	84.79	35.68	3.79	7.63	4.5	94.46
DMM	83.42	12.10	19.53	3.82	6.0	93.25
DMM/ Methanol	82.35	41.87	7.49	12.65	5.0	95.37
DMM/Ethanol	82.27	36.79	5.21	11.38	4.5	92.10
DMM/ Isopropanol	79.33	34.27	2.57	10.50	4.0	91.22
DMM/ 1-Propanol	80.17	31.46	5.20	8.99	3.5	87.49
DMM/ Ethylene glycol	77.49	27.54	4.49	7.29	2.5	85.32
DMM/ Glycerol	76.27	26.03	1.91	9.15	2.0	80.14
DMM/DMSO	74.35	8.38	8.97	1.41	2.5	83.25
DMM/ Methyl formate	76.10	34.44	5.81	3.96	5.5	87.42
DMM/Water	75.23	14.12	16.43	11.88	3.5	89.45

Reaction conditions: bamboo 5 g, solvent 50 g (the weight ratio for the matching-solvents was 1:1), the loading of catalyst is 0.4 wt% of solvent, 200 °C, 120 min.

Therefore, dimethoxymethane can be used as an electrophile to promote the transformation of furfural to 5-hydroxymethylfurfural. Methanol as a reactant can promote the alcoholysis of hemicellulose and cellulose in biomass and suppress both the polymerization of the byproducts (furans/monosaccharides). The -OH in methanol as a nucleophile can actively attack the electrophilic C contiguous to the glycosidic bonds (-OCH<sub>3</sub>, the main bonds between cellulose and hemicellulose basic structural units) with the electron moving to the oxygen strontium ion, which creates neutral hydroxyl groups and good leaving groups by cutting off the C-O bonds. Besides, the acid catalyst can provide reactive H<sup>+</sup>, and the reactive H<sup>+</sup> can activate the oxygen atoms in the glycosidic bonds (-OCH<sub>3</sub>). Therefore, the matching-solvents DMM/METH were introduced into the one-pot directional liquefaction of lignocellulosic biomass.

The acid catalysts could provide hydrogen ions for breaking the β-1,4-glycosidic bonds (-OCH<sub>3</sub>), which are the dominant links between the C5 and C6 monosaccharides units of hemicellulose and cellulose in the biomass. The reactions to investigate the influence of acid catalysts on the conversion of bamboo to MLA were conducted at 200 °C for 120 min. Some typical strong acids C<sub>7</sub>H<sub>7</sub>-SO<sub>3</sub>H, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, and H<sub>2</sub>SO<sub>4</sub> were investigated in the transformation of cellulose and hemicellulose to MLA under DMM/METH matching-solvents. The by-products (furans and glycosides) from cellulose and hemicellulose were also analyzed by GC-MS. Two categories of compounds were the main intermediate transition products of the conversion of cellulose and hemicellulose as described in our previous work with acid

catalysts.<sup>22</sup> It could be hypothesized that the product yield was related to the ability of acidic catalysts to provide hydrogen protons. The results in Table 2 shows that H<sub>2</sub>SO<sub>4</sub> and C<sub>7</sub>H<sub>7</sub>-SO<sub>3</sub>H can offer enough protons to complete the conversion of macro-molecular polymers from bamboo into small molecular products and promote the transformation of byproducts (furans and glycosides) to MLA. H<sub>2</sub>SO<sub>4</sub> is relatively corrosive and difficult to recycle. This above result suggested that C<sub>7</sub>H<sub>7</sub>-SO<sub>3</sub>H is a preferred catalyst for the synthesis of MLA.

**Table 2** Effect of various catalysts on liquefaction of bamboo to MLA.

Catalysts	MLA		Furans yield (%)			Gly yield (%)		Coke yield (wt%)
	Conv. (wt%)	yield (%)	MMF	Furfural	Others	C5-Gly	C6-Gly	
C <sub>7</sub> H <sub>7</sub> -SO <sub>3</sub> H	81.33	41.05	5.19	6.92	1.71	5.18	6.55	18.67
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	80.21	36.37	1.68	4.69	3.62	6.52	5.96	19.79
H <sub>2</sub> SO <sub>4</sub>	82.35	41.87	2.81	3.04	1.65	3.76	8.89	17.65
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	75.33	21.55	5.52	4.87	2.75	11.18	9.27	24.67
AlCl <sub>3</sub>	60.78	17.11	4.15	10.15	0.76	18.53	6.10	39.22
HZSM-5	37.43	10.39	3.45	12.66	3.23	17.45	10.05	62.57
Amberlite IR-20	76.54	18.62	4.79	6.78	5.72	8.43	10.73	23.46
ZrO <sub>2</sub>	48.46	11.18	4.25	11.02	2.89	17.99	13.31	51.54

Reaction conditions: bamboo 5 g, DMM/METH 25 g/25 g, the loading of catalyst is 0.4 wt% of solvent amount, 200 °C, 120 min.

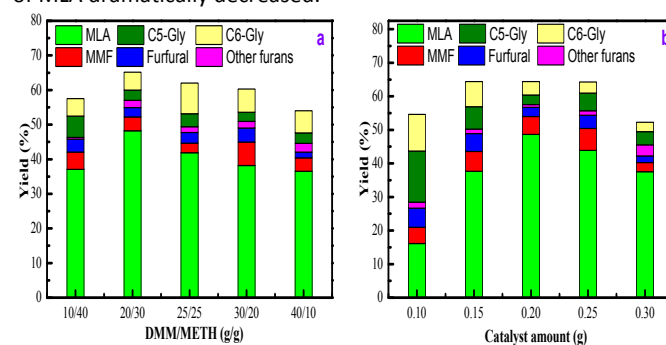
For comparison, Lewis metal salt catalysts Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and AlCl<sub>3</sub> were tested in the transformation of hemicellulose and cellulose to MLA with matching-solvents (DMM/METH). The difference in catalytic performances for AlCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> may also be due to their different Brønsted acidities in DMM/METH media. Surprisingly, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> showed good catalytic performance, and provided a high conversion of bamboo (75.33 wt%) and relative high yield of target product (21.55%). The pH measurement of metal salts' solutions showed that higher MLA yields were always accompanied by lower pH values, which confirmed that Brønsted acidity was an important factor for biomass alcoholysis. Commercial solid acid catalysts (Zeolite catalysts HZSM-5, ion exchange resin Amberlite IR-20, and metal oxide ZrO<sub>2</sub>) were used as the catalyst and lower MLA yields were achieved. The low yields of MLA over HZSM-5 and ZrO<sub>2</sub> maybe due to the small pore size, which could lead to coke formation. The coke can cover the surface of the catalyst (the color of the catalyst changed from white to black brown) and affect the reactivity of HZSM-5 and ZrO<sub>2</sub>. The performance of Amberlite IR-20 was not as expected, and the formation of MLA from bamboo was not ideal. The results from the reaction temperature was high for Amberlite IR-20, and the high temperature can reduce the catalytic activity of molecular sieves or even lead to some inactivation.

Fig.1(a) shows the effect of DMM/METH matching-solvents mass ratio on the formation and distribution of liquefied products at 200 °C. The reaction pathways between converting the C6 and C5 sugars units into MLA were different. As shown in Fig. 1, cellulose and hemicellulose in bamboo is more effectively converted into MLA in the reaction solvents with low DMM/METH mass ratio (methanol rich solvent). The yield of MLA is relatively small in the solvents with high DMM/METH mass ratio (DMM rich solvent). The C6 sugars units in cellulose and hemicellulose can be converted into MLA with methanol alone. However, the conversion of hemicellulose to MLA simultaneously required METH and DMM. The C6 sugar units in cellulose and hemicellulose were converted faster in the matching-solvents with more methanol as compared with the transformation of C5 sugar units in hemicellulose. With the addition of little DMM or methanol (DMM/METH= 10/40 or DMM/METH= 40/10) to the reaction medium, the yields of MLA were less than the large amount of methanol.

The -OH in methanol as a nucleophile can actively attack the electrophilic C contiguous to the β-1,4-glycosidic bonds (-OCH<sub>3</sub>) with the electron moving to the oxygen strontium ion, which creates neutral hydroxyl groups and good leaving groups by cutting off the C-

O bonds between the structural units in cellulose and hemicellulose. Therefore, methanol could react with cellulose and hemicellulose to form methyl hexose glycosides and methyl pentose glycosides. The methyl glycosides were converted into MMF and furfural by alcoholysis. The alcoholic product of cellulose (MMF) is finally converted to MLA in the reaction of methanol. On the other hand, the alcoholic product of hemicellulose (furfural) can react with methanol, becoming DOF. The formation of DOF can destroy the π-conjugation between the carbonyl group and the furan ring, which could make the furan-ring more susceptible to be attacked by the electrophiles and facilitate the subsequent electrophilic substituted reaction process. DMM can be used as the electrophile to promote the transformation of furfural to HMF. More importantly, enough methanol (as solvent) could obviously suppress the polymerization of furfurals. Considering all of the aforementioned results, the optimum composite solvent ratio of DMM/METH was 20/30 and this generated a high MLA yield of 48.20%. Moreover, the DMM/METH mixture was collected and recycled by rotary evaporation (Fig. S2). DMM/METH mixture can be separated with high purity (more than 99 wt%) using extractive dividing-wall column or heat-integrated pressure swing distillation.<sup>23</sup>

Catalyst amounts determine the availability of acidic reaction sites in the solvent and affect the distribution and composition of the product (yields of desirable and undesirable products). The influence of catalyst concentration on the distribution and formation of liquefied products are summarized in Fig. 1(b) and Fig. S3. Increasing the loading of the acid catalyst (C<sub>7</sub>H<sub>7</sub>-SO<sub>3</sub>H), the yields of glycosides, furfurals, and MLA were significantly different. Initially, by increasing the amount of acid catalyst from 0.1 g to 0.2 g, the conversion of bamboo and the yields of MLA were obviously promoted. However, further increase in the amount of catalyst had a negative influence on the yields of target products. The conversions of biomass and yields of MLA dramatically decreased.

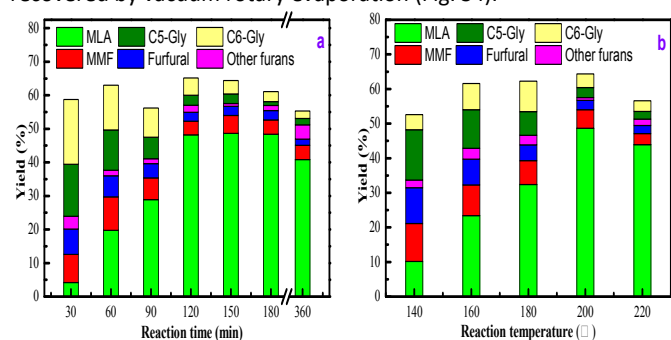


**Fig. 1.** Effect of composite solvent ratio (a) and catalyst amount (b) on the liquefaction of bamboo to MLA.

MLA is the product in the acid-catalyzed conversion of methyl pentose glycosides from hemicellulose and methyl hexose glycosides from cellulose at adequate catalyst concentration. Moreover, the intermediate products and side products of methyl glycosides converted into MLA are mainly furans such as MMF and furfural. Furfural was mainly converted from the alcoholysis of methyl pentose glycoside. MMF was mainly converted from the decomposition of methyl hexose glycoside. At higher acid concentrations, the by-products experience side reactions which increase the contents of side products in the liquefied compounds. Therefore, the addition of excess acid catalyst had a negative influence on the liquefaction process. The higher acid concentrations not only promote the polymerization of intermediate products but also corroded the reactor equipment and hinder economic viability. In general, to achieve good conversions and controllable methanolysis of biomass, an effective catalyst is C<sub>7</sub>H<sub>7</sub>-SO<sub>3</sub>H 0.2 g.

Fig. 2(a) showed the influence of reaction time on the formation of MLA and intermediate compounds from bamboo in the composite matching-solvents. At the beginning of the experiment, the operating time ranged from 30 to 180 min. When the operating time prolonged

from 30 to 120 min, the conversion of bamboo was around 83 wt% to 86 wt%, and the yield of MLA increased from 4.17% to 48.20%. When the holding time further increased, more C6 sugar and C6 sugar substrates from hemicellulose and cellulose were transformed into MLA, and the highest yield of MLA was obtained (48.68%) at a reaction time of 150 min. This result indicated that the optimal reaction time is 150 min. As the reaction time increased more than 150 min, the conversion of bamboo approximate 85 wt%. When the reaction time was more than 150 min, the yield of MLA and the conversion of bamboo declined gradually over time. In general, prolong the reaction time may lead to the polymerization of the liquefied products. Moreover, mostly matching-solvents were recovered by vacuum rotary evaporation (Fig. S4).



**Fig. 2.** Effect of different reaction time (a) and temperature (b) on the liquefaction of bamboo to MLA.

The liquefaction temperatures ranged from 140 to 220 °C at intervals of 20 °C (Fig. 2(b) and Fig. S5). When the operating temperature prolonged from 140 to 200 °C, the yield of MLA significantly increased and grew from 10.17% to 48.68%. At or above 180 °C, which is the softening temperature of hemicellulose and cellulose. Heating and acid catalyst may bring the rotation of polar -CH<sub>2</sub>OH groups in the hemicellulose and cellulose network resulting in breaking of polysaccharide chains and promote the formation of C5-Gly and C6-Gly. At temperatures higher than 180 °C, the sub-critical methanol could provide good solubility for the liquefied products and a high auto-genetic pressure during the reaction, which could promote the transformation of biomass to MLA. When the reaction temperature was 200 °C or 220 °C, the yield of MLA was more than 43.90%. This indicated that as the temperature approached the critical point of methanol, the reactivity and diffusion of methanol was significantly improved. When the temperature increased above 200 °C, the yields of MLA began to decrease due to more side-reactions (the polymerization of products) at higher temperatures. After the stepwise extraction and precipitation of the liquefied products under optimal reaction conditions (Fig. S6), the absolute content of the extracted methyl levulinate was up to 88% (Fig. S7). The DMM/METH solvents were recovered and separated with extractive distillation to be used in subsequent experiments (Fig. S8).

The intermediate products of the liquefaction process include furans and glycosides compounds, and they were identified with GC-MS during the liquefaction process of biomass to MLA. To study the reaction path for the conversion of bamboo material to MLA in DMM/METH matching-solvents with acid catalyst, various pentose and hexose carbohydrates such as xylose, glucose, methyl xyloside (MLX), methyl glycoside (MLG), pentosan, and microcrystalline cellulose (MCC) were selected as the models for the directional liquefaction under the optimal reaction condition. Table 3 shows the formation of MLA from different model compounds under DMM/METH, and these carbohydrates provided differing yields of MLA.

The MLA yields from MCC (33.87%) was significantly lower than that from glucose (62.8%) and methyl glycoside (60.2%) under the same reaction conditions (180 °C). Compared to hexose monosaccharide, the glucose units in MCC molecules are relatively

difficult to break because the units are strongly linked among the highly polymerized cellulose chains. The MCC with high crystallinity and degree of polymerization is insoluble in the DMM/METH medium, which leads to poor substrate accessibility to the solvent and catalyst. The MLA yields from pentosan (26.94%) was also significantly lower than that from xylose (43.50%) and methyl xyloside (53.87%) under the same reaction conditions (180 °C). This result may be due to the dissolved state of pentosan in DMM/METH matching-solvents medium, and the pentosan was easily converted into methyl xyloside as the intermediate product during the methanolysis reaction with the acid catalyst. Moreover, when MLG and MLX were used as the model compound, the yields of MLA were higher than that from glucose and xylose. It may be summarized that the reaction pathway from xylose, glucose, pentosan, and MCC to MLA involves intermediate transition state compounds (methyl glucoside or methyl xyloside).

**Table 3** Target products yields for various models in the liquefaction.

Materials	T (°C)	Conv. (wt%)	MLA yield (%)	Intermediate product yield (%)					
				C5-Gly	C6-Gly	Furfural	HMF	MMF	DMF
Xylose	140	99.27	23.27	0.73	–	5.69	1.32	4.78	0.69
	160	100	43.50	–	–	7.54	2.50	6.22	1.34
	180	98.39	37.81	1.61	–	8.94	1.59	5.92	2.01
Glucose	140	100	34.70	–	24.31	–	3.24	8.69	0.43
	160	100	62.80	–	15.90	–	3.80	7.44	1.33
	180	99.45	49.57	–	0.12	–	4.78	7.02	0.98
MLX	160	99.89	40.24	0.11	–	4.98	4.21	1.35	0.54
	180	99.32	53.87	0.68	–	7.62	2.04	2.25	1.03
MLG	160	99.5	51.46	–	0.5	–	2.07	9.21	2.31
	180	100	60.20	–	–	–	3.21	11.47	1.98
Pentosan	180	93.19	22.32	6.81	–	8.76	4.35	1.22	2.21
	200	95.38	26.94	4.62	–	5.23	5.71	0.58	1.89
MCC	180	89.17	33.87	–	9.32	–	2.75	5.49	2.90
	200	86.42	46.40	–	11.32	–	1.67	7.03	0.78

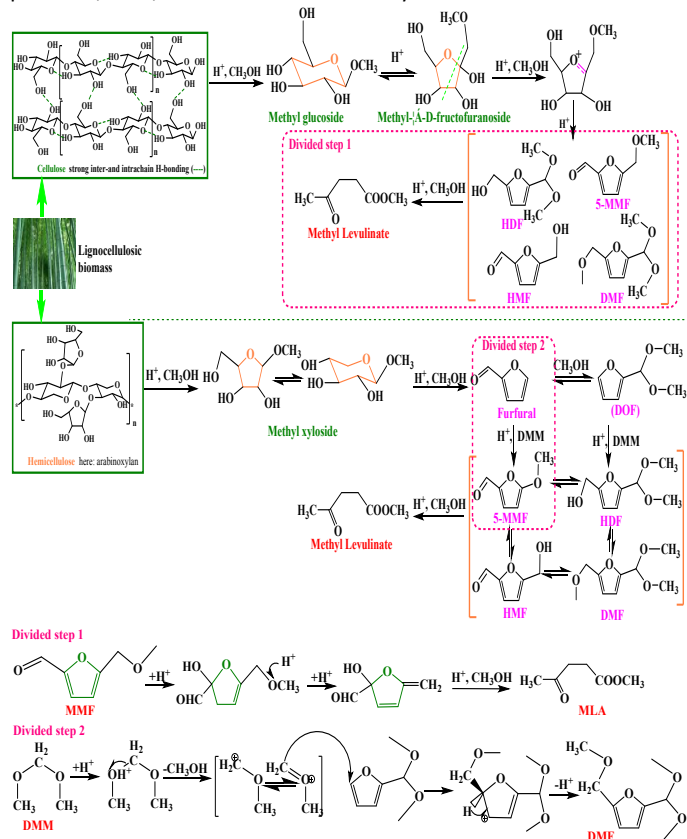
Reaction conditions: material 5 g, solvent 50 g (the weight ratio for the matching-solvents was 1:1), the concentration of catalyst 0.4 wt% (basis of solvent amount), 120 min.

We proposed the mechanism of C6 and C5 conversion to MLA by GC-MS to identify the intermediate transition state compounds and products (Fig. S9 and Fig. S10). The composition and distribution of intermediate compounds in the directional liquefaction was also investigated in detail (Fig. S12 and Fig. S13). In the first place, we detected that furfural and 5-hydroxymethylfurfural are main intermediates in the conversion of C6 and C5 to methyl levulinate (MLA) by GC-MS and HPLC-MS. In the process of directional liquefaction in DMM/METH solvents, the C6 sugars mainly reacted with methanol and converted to methyl levulinate. The specific reaction process is shown in Fig. S14. Hemicellulose in biomass is mainly composed of five carbon sugars linked by glycosidic bonds. The hemicellulose was directly converted into the intermediate methyl xyloside, and then transformed into furfural (Fig. S15).

The structures for cellulose and hemicellulose are merely pictorial and do not imply a particular sequence. The possible reaction route for the directional liquefaction of bamboo with DMM/METH as matching-solvents was based on the GC-MS results. Cellulose in biomass is made up of glucose units linked by  $\beta$ -1,4-glycosidic bonds. Fig. 3 shows that cellulose was first transformed into methyl glycoside and further converted into MMF or HMF, and then MMF or HMF can be further converted into MLA and methyl formate. Hemicellulose in biomass is mainly composed of five carbon sugars linked by glycosidic bonds. The hemicellulose was directly converted into the intermediate methyl xyloside and then transformed into furfural. Therefore, furfural is an important intermediate for the conversion of hemicellulose to levulinate.

The differences in structure between furfural (the dehydration intermediate of C5 sugars to MLA) and MMF (the dehydration

intermediate of C6 sugars to MLA) is the additional hydroxymethyl group in HMF. If the methyl and hydroxyl groups were joined in the furan ring of furfural, furfural could be converted into HMF, and subsequently converted into levulinic ester/acid. The furan ring in furfural has aromaticity and can possibly introduce the hydroxymethyl group in furfural via an electrophilic substitution process. DMM can be used as an electrophile to promote the transformation of furfural HMF via electrophilic substitution reaction. Besides, methanol as a reactant plays multiple critical parts, as methanol can promote the alcoholysis of hemicellulose and cellulose in biomass and suppress the polymerization of the byproducts. With this method, both the C5 sugars derived from hemicellulose and C6 sugars derived from the cellulose can be converted into the same products, MLA, with the same acid catalyst.



**Fig. 3.** Possible reaction route for directional liquefaction of biomass to MLA in DMM/METH.

In summary, we have developed a new and efficient solvent system for the synergistic conversion of C6 and C5 sugars in cellulose and hemicellulose to methyl levulinate. The new pathway for the directional and one-pot simultaneous conversion of hemicellulose and cellulose in biomass into methyl levulinate has been demonstrated with DMM/METH as matching-solvents. The matching-solvents improved the liquefaction process and the high yield of MLA (48.68%) could be obtained from bamboo. This synergistic catalytic conversion of biomass is an effective method that can produce high yields of added-value chemical from biomass.

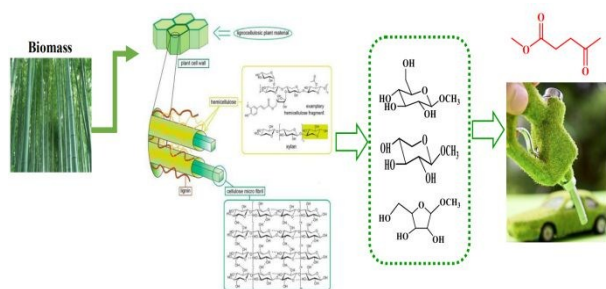
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