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Methyl 4-methoxypentanoate: a novel and potential downstream chemical of biomass derived gamma-valerolactone

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Lignocellulosic derived gamma-valerolactone was effectively converted into methyl 4-methoxypentanoate, a potential liquid biofuel, solvent and fragrance, by the catalysis of hydrogen exchanged ultra-stable Y zeolite (HUSY) and insoluble carbonates such as CaCO₃. The catalytic competing generation process between methyl 4-methoxypentanoate and pentenoate esters was also analysed.

The worldwide consumption in transportation and chemical industry, which strongly depends on fossil resources, has given rise to the problems of resource shortage coupled with global warming, environmental deterioration, serious political issues and military crisis. Lignocellulosic biomass, as a sustainable and renewable carbon source, is being studied for the production of fuels and chemicals which are comparable with that derived from oil and coal. The carbohydrates derived from biomass can be converted into various platform molecules, such as furfural, 5-hydroxymethylfurfural (5-HMF), levulinate acid (LA) and levulinate esters.

In recent years, a lot of attention has been given to gamma-valerolactone (GVL), a platform molecule which could be synthesized from LA or ethyl levulinate using diverse hydrogen sources [1-3], because it's recognized as a potential fuel additive, green solvent and promising precursor for other downstream chemicals, such as liquid hydrocarbons for fuel application [4,5]. Simultaneously, a fair amount of previous reports have been focused on the synthesis of pentenoate esters, pentenoate esters and bio-based nylon monomers from GVL in the presence of methanol (or ethanol) and acid catalysts [6-12]. The main products could be categorized into unsaturated fatty acid esters including methyl 2-pentenoate (M2P), methyl 3-pentenoate (M3P) and methyl 4-pentenoate (M4P) which could be hydrogenated to methyl pentanoate (MP), and unexpected by-products such as methyl 4-methoxypentanoate (MMP), as concluded in Scheme 1. MMP, which has been regarded as a by-product of the reaction, occupies a yield of 5-20% [6], has more potential to be applied as fuel additive, bio-oxygenated solvent [13], medical intermediate and fragrance than GVL and pentenoate esters owing to its advantageous properties such as water insolubility and high heat-value. In this study, MMP was produced, for the first time as we know, in a rather high conversion and selectivity in methanol with high GVL loadings in the presence of Hydrogen exchanged ultra-stable Y zeolite (HUSY) and CaCO₃ (Scheme 1).

Scheme 1 The synthesis of pentenoate esters and MMP from GVL and alcohols
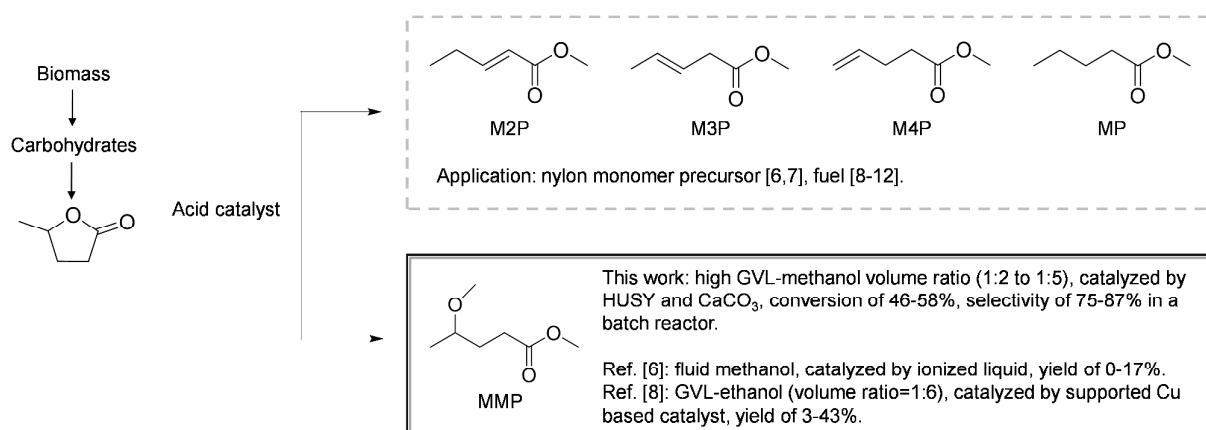
In our previous study on the liquefaction of biomass in GVL-methanol solvent, we accidentally found that the ash components in biomass could signally improve the yield of MMP in GVL ring-opening reaction under 3 MPa nitrogen (at RT) with the catalysis of HUSY. After a series of strict experiments, CaCO₃, a common insoluble carbonate, was discovered to be the key compound in the ash content which effectively promoted the generation of MMP, while other salts and oxides in the ash, such as KCl, K₂CO₃, NaCl, SiO₂, Al₂O₃, were found to be ineffective. With the catalysis of several acidic zeolites and CaCO₃, the product

distribution of the ring-opening reaction of GVL in methanol with a quite high GVL-methanol ratio (1:2 v/v) were classed into three categories: pentenoate esters, MP and MMP, as summarized in Table 1 and Figure S1. It is noted that USY zeolite showed higher activity in the conversion of GVL to form MMP, among which hydrogen exchanged ultra-stable Y zeolite (HUSY) was chosen as acid catalyst in this research because of its relatively higher activity under given conditions. The percentage conversion of GVL was 46.4%, which is rather high in consideration of the enlarged amount of substrate under a sealed condition in this research (1:2 v/v). There was only a little M2P generated during the reaction, which was consistent with the result given by Zeng[6], suggesting that the rearrangement reaction rarely occurred among α-C, β-C and γ-C. Besides, two *cis-trans*-isomers of M3P, *E*-M3P and *Z*-M3P, with different retention times and a relative amount of approximately 2:1, were identified by GC-MS (Figure S1). Additionally, the ratio of M3P and M4P in every experiment ranged between 2:1 and 4:1, implying that the reaction obeyed Saytzeff rule. It was also determined that other zeolites with sufficient acidity might also be effective for the ring-opening reaction of GVL, such as HY (Table 1, Entry 1).

Table 1 The product distruibution of ring-opening reaction of GVL catalyzed by solid acids and $CaCO_3$

Entry	Catalyst	Conversion (%)	Selectivity to pentenoate esters (%)			MP (%)	MMP (%)
			M2P	M3P	M4P		
1	HY	32.6	-	12.3	5.9	6.9	74.8
2	HZSM-5	14.4	-	38.2	11.7	10.2	39.8
3	USY	20.8	-	6.9	5.7	11.5	75.9
4	HUSY	46.4	-	8.5	5.2	7.3	78.9
5	SO_4^{2-}/USY	40.1	4	35.5	12.9	9.7	37.6

Reaction conditions: 10 mL GVL, 20 mL methanol, 0.5 g zeolite, 0.5 mmol $CaCO_3$, 250 ^{o}C, N_2 (3 MPa, RT), 700 rpm, 4 h.

Detailed optimization has been conducted to achieve higher MMP yield, as shown in Table 2. Prolonged reaction time from 1 to 4 h and proper temperature benefited the conversion of GVL, while the selectivity to MMP was not changed much (Table 2, Entry 6, 11, 12 and 13). However, when the reaction time was prolonged to 12 h, the selectivity to MMP was dramatically reduced from 78.9% to 45.7% (Table 2, Entry 6, 14). Simultaneously, the conversion of GVL was a little higher, while the selectivity to pentenoate esters was up to 49.9% probably as a result of chemical equilibrium which will be discussed later. Moreover, no obvious effect has been observed by enlarging the add amount of methanol or HUSY (Table 2, Entry 7 and 8). As Entry 9 showed, when the dosage of $CaCO_3$ was double, the conversion percentage of GVL and selectivity to MMP were increased to nearly 60% and 90%, observably more than those of Entry 7 and 10. Otherwise, the recycle performances of catalyst have also been tested. As shown in Table S1, the catalytic activity of used catalyst could be recovered by calcining. MMP produced in the enlargement experiment of Entry 10 was separated by vacuum distillation and characterized by GC-MS and ^{13}C-NMR (Figure S2, S3). Physical and chemical properties of MMP were studied and presented in Table S2, which provide considerable potential of MMP as a fuel additive and solvent.

Table 2 Catalytic conversion of GVL to MMP under different reaction conditions

Entry	Feed ratio[a]	Temperature (^{o}C)	Reaction time (h)	Conversion (%)	Selectivity (%)	
					Pentenoate esters	MMP
6	1:2	250	4	46.4	13.7	78.9
7	1:5	250	4	50.7	21.3	70.5
8	1:2[b]	250	4	40.9	44.0	47.4
9	1:5[c]	250	4	57.9	6.3	87.1
10	1:5[d]	250	4	43.5	17.3	75.5
11	1:2	200	4	37.9	6.2	76.8
12	1:2	250	1	40.0	9.9	76.7
13	1:2	250	2	44.0	10.1	82.0
14	1:2	250	12	53.0	49.9	45.7

Reaction conditions: 0.5 g HUSY, 0.5 mmol $CaCO_3$, N_2 (with an initial pressure of 3 MPa, RT), 700 rpm. [a] The volume ratio of GVL and methanol. [b] The amount of HUSY was increased from 0.5 g to 0.8 g. [c] The amount of $CaCO_3$ was increased from 0.5 mmol to 1 mmol. [d] The total amount of GVL, methanol, HUSY and $CaCO_3$ was 5 times of those in entry 9.

It is quite interesting why $CaCO_3$ showed such excellent catalytic activity in the generation of MMP. In order to study the mechanism, various carbonates and calcium salts were employed to verify the effective ingredient (Ca^{2+} or CO_3^{2-}). As Entry 16 in Table 3, GVL conversion of 44.8% was reached when HUSY was applied alone, but only 19.0% of which contributed to MMP while 75.2% to pentenoate esters. Compared with that proceeded with no catalyst in Entry 15 or with $CaCO_3$ alone in Entry 17, less than 15% GVL was consumed, mainly alcoholyzed to form MP and gave only a small amount of MMP. As such, it could be deduced that the formation of pentenoate esters strongly depended on HUSY, which effectively catalyzed the ring-opening reaction and dehydration process of GVL. Similarly, no pentenoate ester was detected when soluble alkalis such as Na_2CO_3, K_2CO_3 and CaO (Table 3, Entry 18-20) were adopted, indicating that HUSY was totally disabled by the alkalis as the mechanism given in Scheme S1. The addition of insoluble carbonates, such as $BaCO_3$ and $MnCO_3$ (Table 3, Entry 22, 23) showed no harm for HUSY, thus leading to similar GVL conversion and selectivity to MMP as compared with that of in the presence of $CaCO_3$. On the contrary, experiments conducted with calcium oxide and salts (Table 3, Entry 20, 24 and 25) didn't give high yields of MMP, suggesting that Ca^{2+} was not the key factor for the reaction. In conclusion, insoluble carbonates, as trace CO_3^{2-} donors, played an important role in the synthesis of MMP in the premise that HUSY existed.

Table 3 The effects of carbonates and calcium salts in the synthesis of MMP

Entry	Catalyst	Conversion (%)	Selectivity (%) Pentenoate esters	MP	MMP
15	-	14.6	-	94.5	1.6
16	HUSY	44.8	75.2	4.2	19.0
17	$CaCO_3$	14.8	-	95.7	4.3
18	HUSY+K_2CO_3	17.8	-	92.3	7.7
19	HUSY+Na_2CO_3	15.0	-	88.1	11.8
20	HUSY+CaO	12.0	-	27.7	72.3
21	HUSY+$CaCO_3$	46.4	13.7	7.3	78.9
22	HUSY+$BaCO_3$	40.1	4.7	18.3	77.0
23	HUSY+$MnCO_3$	46.4	3.4	16.9	79.1
24	HUSY+$CaSO_4$	35.7	83.4	4.2	10.4
25	HUSY+$CaCl_2$	8.4	-	42.2	57.8
26	HUSY+CH_3ONa[a]	52.2	9.3	8.1	82.1
27	HUSY+CO_2[b]	43.1	36.4	3.6	60.0

Reaction conditions: 10 mL GVL, 20 mL methanol, 0.5 g HUSY, 0.5 mmol carbonates, oxide or salts, 250 ^{o}C, N_2 (with an initial pressure of 3 MPa, RT), 700 rpm, 4 h. a: 60 μL of CH_3ONa solvent (in methanol, 5 mol/L) was added. b: CO_2 (about 80 mL, 1 bar, RT) was purged into the reactor followed by pressurizing to 3 MPa by N_2. The solvent was 19 mL methanol and 1 mL H_2O.

Although $CaCO_3$ showed significant effect on the generation of MMP from GVL, it was still confused that there was an inverse correlation between the amount of MMP and pentenoate esters, which suggested that pentenoate esters or MMP might be generated successively or competitively. To investigate this issue, gamma-butyrolactone (GBL) was chosen to conduct a model reaction under the same conditions. Interestingly, although 56.8% GBL was converted in the presence of HUSY and $CaCO_3$ to form methyl 4-methoxybutyrate (MMB, major product), a little 4-methoxybutyric acid and 4-hydroxybutyrate, no butenoate esters was detected in the product (see the GC spectra in Figure S4), which indicated that there was no carbocation generated. Hence, the formation of MMB from GBL was subjected to a S_N2 process (Scheme 2a), implying that the methoxy group was not from the addition reaction on the double-bonds of butenoate esters, which was also applicable to that of GVL.
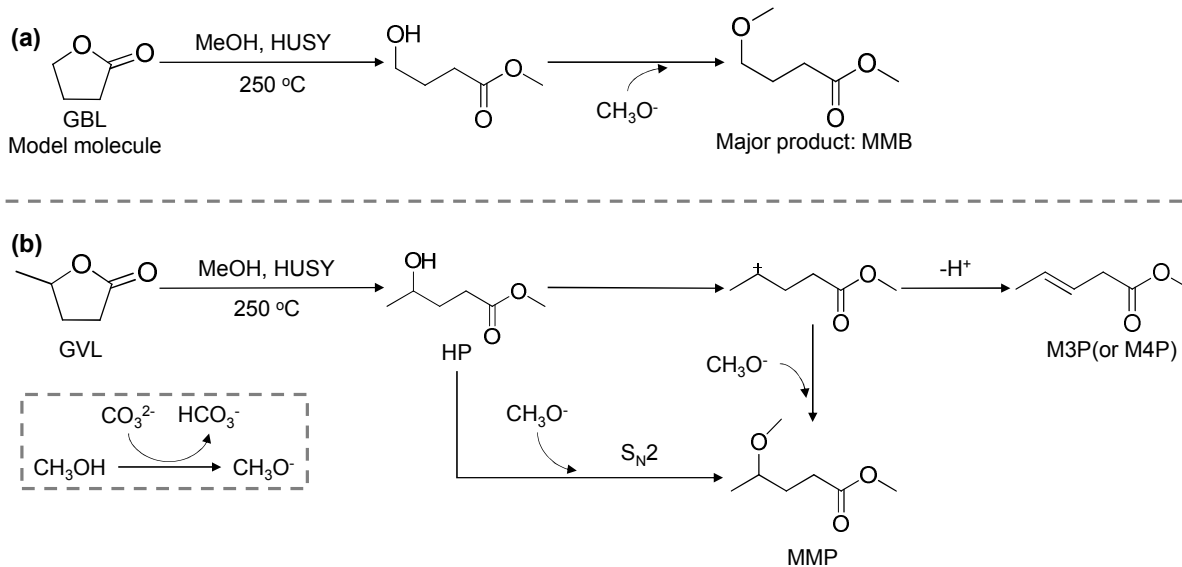
Scheme 2 (a) A model reaction conducted with GBL as reactant; (b) the competing reactions in the formation of MMP from GVL

With respect to 4-hydroxypentanoate (HP, which can be considered as a secondary alcohol), the ring-opening intermediate of GVL, it was feasible for the hydroxyl group to be protonated and then dehydrated under the catalysis of HUSY to form secondary carbocation followed by E1 elimination pathway to generate pentenoate esters, as shown in Scheme 2b. Meanwhile, a little MMP might be produced with the presence of methoxy anion from the self-ionization of methanol. However, HP could not be detected by GC-MS as a thermal instable intermediate, which was quickly converted into GVL or other products at high temperature [14]. When $CaCO_3$ was introduced, it was supposed that the generation of methoxy anion (as the dotted box in Scheme 2b), a strong nucleophile, was thus promoted, and then induced the addition reaction of carbocation to form MMP. Furthermore, enriched methoxy anions could also greatly enhance the S_N2 substitution

process of HP, which led to a significant increase of selectivity to MMP from less than 20% to nearly 80% (Table 3, Entry 16, 21). Meanwhile, a slight increase of GVL conversion was also observed (Table 3, Entry 14 and 19-21). The assumption was further verified by introducing CH_3ONa or CO_2 in place of $CaCO_3$ (Table 3, Entry 26-27, and Table S3). Satisfying GVL conversion and MMP selectivity were obtained, proving the importance of CO_3^{2-} and methoxy anion.

However, it was remarkable that there existed a dynamic equilibrium between GVL and MMP, because the GVL conversion could hardly be improved much by prolonging the reaction time in a sealed reactor (Table 2, Entry 14). The reason of the selectivity to pentenoate esters could be increased obviously was that the E1 elimination reaction of HP was irreversible, which was in accordance with that Zeng has proved [6].

Conclusions

In summary, the selectivity of GVL ring-opening reaction to MMP could be greatly improved from less than 20% up to nearly 90% by the addition of $CaCO_3$ or other insoluble carbonates. The anion, CO_3^{2-}, was proved as the active species to promote the generation of CH_3O^- which acted as nucleophile to attack HP derived from the ring-opening reaction of GVL to produce MMP by S_N1 or S_N2 procedure in competition with pentenoate esters. Meanwhile, a supposed mechanism of the competing reaction was also provided. Ongoing work will be focused on the downstream application of MMP for value added molecule production.

Notes and references

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