Towards 'bio-based' Nylon: conversion of γ-valerolactone to methyl pentenoate under catalytic distillation conditions

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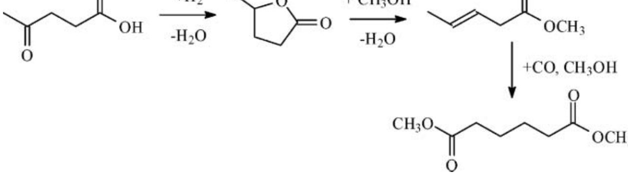
Methyl pentenoate, a promising Nylon intermediate, is produced in >95% yield *via* the transesterification of γ-valerolactone, a bio-based intermediate, under catalytic distillation conditions.

The chemical industry has relied on crude oil as a major feedstock for more than half a century. As the oil fields are maturing, crude oil is becoming increasingly difficult to produce at a rate that meets demand. The threat of an oil shortage has stimulated the search for alternative fuels and chemical feedstocks, for example natural gas, coal or biomass.

Several studies were recently devoted to identifying biomass derivatives that could become platform molecules for the chemical industry.[1] One of them is levulinic acid, which is produced *via* the acid hydrolysis of cellulosic materials.[2] Previous work suggested that levulinic acid could be converted into caprolactam or adipic acid, which are high value Nylon intermediates.[3] According to Scheme 1, the conversion could proceed *via* the hydrogenation of levulinic acid to γ-valerolactone (GVL),[4] a subsequent transesterification to methyl pentenoate[5] and, finally, a hydroformylation, hydrocyanation or hydroxycarbonylation to caprolactone, caprolactam or adipic acid.[6] This novel route to Nylon intermediates could be of great significance to the chemical industry, for the present routes are notoriously inefficient in terms of energy and chemical usage.[7]

We report here a novel and efficient approach to the transesterification of γ-valerolactone to methyl pentenoate that is based on catalytic distillation and one that alleviates the major drawbacks of the gas-phase approaches reported so far.[5] Indeed, reproduction of the gas-phase reaction based on an acidic H-ZSM-5 catalyst[5b] revealed significant amounts of pentenoic acid and dimethyl ether as coproducts at 300 °C. The alternative process, based on a Cs/SiO_2 catalyst, requires severe conditions (350–400 °C) and still proceeds at a low production rate ($\sim$0.1 $g_{product}\ g_{cat}^{-1}\ h^{-1}$).[5c]

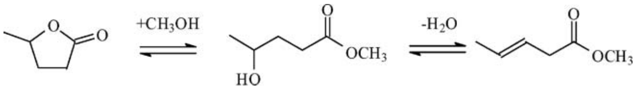


Scheme 1 Conversion of levulinic acid to dimethyl adipate.

The present catalytic distillation approach exploits the large difference in boiling point between γ-valerolactone (207 °C) and methyl pentenoate (127 °C) to shift the thermodynamic equilibrium towards the product. Thermodynamic calculations‡ indeed revealed a free energy change of reaction ΔG of some +1.5 kJ mol^{-1} for the overall reaction, *i.e.* about +1.0 and +0.5 kJ mol^{-1} from the formation and conversion of the hydroxy pentenoate intermediate, respectively (Scheme 2). A mechanism based on the ring-opening of the lactone to pentenoic acid followed by esterification is less likely as the ring-opening proceeds with an unfavorable ΔG of +25 kJ mol^{-1}.

In the present study, the reaction was performed in fed-batch mode, with methanol being continuously fed into a distillation flask charged with γ-valerolactone and the acid catalyst. The distillate product, consisting of unconverted methanol, methyl pentenoate and water, was continuously removed *via* a small, insulated rectification column. An N_2 stream was also applied to strip out the product. Further details are reported in the experimental section below.§

In a typical experiment with *para*-toluene sulfonic acid (pTSA) as the catalyst (Fig. 1), methanol was slowly fed into the flask while the reaction medium boiled at $\sim$200 °C. A mixture of methanol, $\sim$40 wt% methyl pentenoate and water distilled off, and



Scheme 2 Conversion of γ-valerolactone to methyl pentenoate.

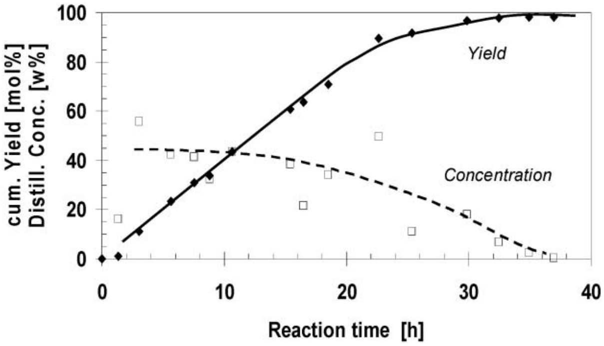


Fig. 1 Transesterification of γ-valerolactone with methanol to methyl pentenoates (200 °C, lactone : pTSA = 50 : 1 molar ratio; MeOH feed rate = 11 mol $mol_{pTSA}^{-1}\ h^{-1}$).

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condensed at ~90 °C at the top of the rectification column. The yield of methyl pentenoate collected over consecutive distillate fractions (called 'cumulative yield' in Fig. 1) increased almost linearly with time up to ~80 mol%. The production rate remained fairly high at 2.0 $\text{mol}_{\text{product}}\ \text{mol}_{\text{cat}}^{-1}\ \text{h}^{-1}$ or 1.3 $\text{g}_{\text{product}}\ \text{g}_{\text{cat}}^{-1}\ \text{h}^{-1}$ for most of the run. As the reaction approached completion, the temperature of the reaction medium was raised to 230–250 °C and the pentenoate content of the distillate (labelled 'distillate concentration' in Fig. 1) dropped from ~40 wt% to zero. At that point, the yield of methyl pentenoates had reached 98%. The esters consisted of a mixture of various isomers, namely the pent-4-enoate (25–35%), the *cis*/*trans* pent-3-enoates (65–75%; mainly the *trans*-isomer) and the *cis*/*trans* pent-2-enaotes (1–5%). The distribution of these isomers changed slightly with time and conversion. Traces of pentenoic acid isomers were the only side products detected in the distillate. No dimethyl ether could be detected in the N_2 purge stream, even upon passing it through a liquid N_2 trap. The reaction residue consisted mainly of the methyl ester of the pTSA catalyst, with small amounts of methyl pentenoates and impurities that were present in the feed.

Variations in reaction conditions affected the production rate and concentration of methyl pentenoate in the distillate. For instance, the production rate was reduced upon diluting the γ-valerolactone with sulfolane but remained unaffected by changes in catalyst loading or methanol feed rate. The concentration of methyl pentenoate in the distillate increased upon increasing the catalyst loading and upon decreasing the methanol feed rate.

Substituting methanol for higher alcohols resulted in lower yields of the corresponding pentenoate esters. The reaction proceeded to lower conversion and was accompanied by the formation of heavy products and some ethers (Fig. 2). This trend is most likely due to the increased difficulty of withdrawing the heavier alkyl pentenoates from the reaction medium by means of distillation.

The benefit of distilling the ester was further confirmed by a batch experiment, in which γ-valerolactone, methanol and pTSA were reacted for 22 h at 200 °C. The product contained no more than 4 mol% methyl pentenoates, with traces of pentenoic acid and dimethyl ether. This low yield could not be explained by a degradation of the pentenoate esters during the batch experiment, since it did not react during complementary batch experiments with methyl pentenoate and pTSA in the presence or absence of γ-valerolactone.

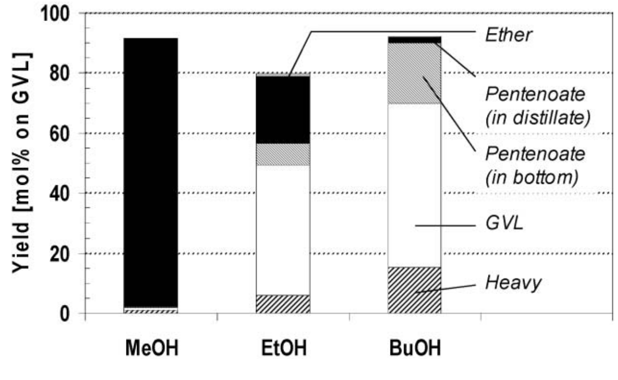
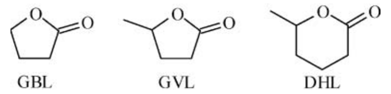


Fig. 2 Composition of the bottom and top product of the transesterification of γ-valerolactone with alcohols to alkyl pentenoates (after 25 h at 200 °C with 100 mol GVL, 3 wt% pTSA and alcohol feed rates of 25, 15 and 10 mol h^{-1} for MeOH, EtOH and BuOH, respectively).



Scheme 3 Lactone feedstock.

Attempts to produce pentenoic acids by co-feeding water instead of alcohols provided yields of 2–4 mol% after 7 h, depending on the water feed rate. In this case, again, the product has too high a boiling point (196–206 °C) to be easily distilled from the reaction medium. Moreover, the reaction is thermodynamically unfavorable, as mentioned above.

Substituting γ-valerolactone (GVL) by other lactones encountered mixed success (Scheme 3). δ-Hexanolactone (DHL) was converted to the target methyl hexenoates with 70 mol% yield and ~80 wt% distillate concentration. Like γ-valerolactone, this lactone leads to a hydroxy ester intermediate with a secondary hydroxyl group that is easily eliminated under acidic conditions. In contrast, the γ-butyrolactone (GBL), which leads to a primary hydroxy-ester, formed the target methyl butenoates in trace amounts and produced many oligomeric products.

Several acidic and basic catalysts were also investigated under these conditions. All acidic catalysts tested, whether homogeneous or heterogeneous, showed some activity in this reaction. As reported in Table 1, H_2SO_4 showed the highest initial activity, followed by pTSA. Heterogeneous catalysts were also active, with the initial activity (based on weight and H^+) decreasing in the order of their acid strength, *i.e.*

$$\text{Nafion NR50} > \text{zeolites} > \text{amorphous silica alumina (ASA)}$$

It should be noticed that the Nafion and zeolites were more active than the homogeneous acids when expressed per proton. The Nafion NR50 is a strongly acidic resin. The zeolites include a medium-pore H-ZSM-5 and two large-pore H-Beta zeolites, having Si/Al atomic ratios of 15, 10 and 100, respectively. Interestingly, the pore size and Si/Al ratio seem to have a limited effect on the initial activity of the zeolite. All acidic catalysts showed a comparable distribution of pentenoate isomers, a comparably low coproduction of pentenoic acid and negligible formation of diethyl ether or heavy products.

Amphoteric or truly basic catalysts, such as γ-alumina, La-doped γ-alumina and KOH, showed no significant activity in producing methyl pentenoate or in converting γ-valerolactone to any significant level. Such catalysts are known to be active in transesterification reactions. Their lack of activity here is most likely due to their inability to dehydrate the hydroxy ester intermediate under these mild conditions (Scheme 2).

In summary, the present work reports the possibility of converting γ-valerolactone and methanol to methyl pentenoate, under mild conditions using strong acid catalysts, when performed under catalytic distillation conditions. The reaction produces a distillate that is rich in methyl pentenoates, alongside methanol, water and minute amounts of pentenoic acid. The methyl pentenoates can be further converted to nylon intermediates such as adipic acid, dimethyl adipate or caprolactam. This provides an efficient route for producing Nylon polymers from renewable feedstock.

Table 1 Performance of catalysts (200 °C, catalyst loading = 1–7 wt% on GVL, MeOH feed rate = 0.23 mol mol_{GVL}^{-1} h^{-1}

			Initial production rate	
Catalyst	H^+/ mmol g^{-1}	Catalyst loading (wt%)	/g g_{cat}^{-1} h^{-1}]	/mol $mol_{H^+}^{-1}$ h^{-1}
		Homogeneous acid		
H_2SO_4	10.2	1.6	3.4	2.9
pTSA	5.8	3.0	1.5	2.3
$La(OTf)_3$	1.7	1.3	0.2	1.0
		Heterogeneous acids		
Nafion NR50	0.12	2.9	2.6	190
H-ZSM-5 (15)	1.0	4.2	1.3	11
H-Beta (10)	1.5	5.6	0.9	5.3
H-Beta (100)	0.16	5.3	0.9	49
ASA	0.5	2.9	0.1	1.8
		Amphoters and bases		
Al_2O_3	—	5.0	0.0	0.0
16% La/Al_2O_3	—	6.6	0.0	0.0
KOH	—	1.8	0.0	0.0

Notes and references

‡ The thermodynamic calculations were based on ideal gases at room temperature and were limited to the formation of the *trans* pent-3-enoate isomer. The coproduction of the four other isomers would obviously decrease the $\Delta G_{reaction}$.

§ **Experimental section**: The reaction was performed in a 250 mL three-necked flask equipped with a small rectification column, a water-cooled condenser and a collection flask. The reaction flask was loaded with 160 g γ-valerolactone and 1–5 g acid catalyst, heated up to 200 °C and fed with methanol at 0.1–0.5 mL min^{-1} under an N_2 stripping flow of 10 mL min^{-1}. The product was condensed in two stages. The first stage was condensed at room temperature. The uncondensed gas stream was subsequently passed through a second condensation stage at −78 °C using an acetone/CO_2 bath. The product was analyzed by GC and GC-MS. The mole balance typically closed at ~90 mol%, based on the lactone.

The chemicals were of analytical grade and were used without pre-treatment. The catalysts were commercial products. Prior to use, the zeolites, Nafion, ASA and alumina materials were dried at 150 °C.

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