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Abstract: The present work explored a catalytic transfer hydrogenation process with several supported noble metal on carbon as catalysts for the production of γ-valerolactone (GVL) from methyl levulinates (ML) in iso-propanol (2-PrOH) and the performance of the commercial 5%Ru/C in continuous flow were investigated, GVL yields up to 83% at 150ºC (40 bar) using a high load (0.4 M ML) feed at 0.8mL/min flow rate. The catalyst productivity (Pr) equal to 0.99 mol g^{-1} h^{-1}. Methyl 4-hydroxypentanoate (MHP) were produced as major side product in lower amounts in continuous flow mode. Long-term (9h) catalyst stability experiment showed good

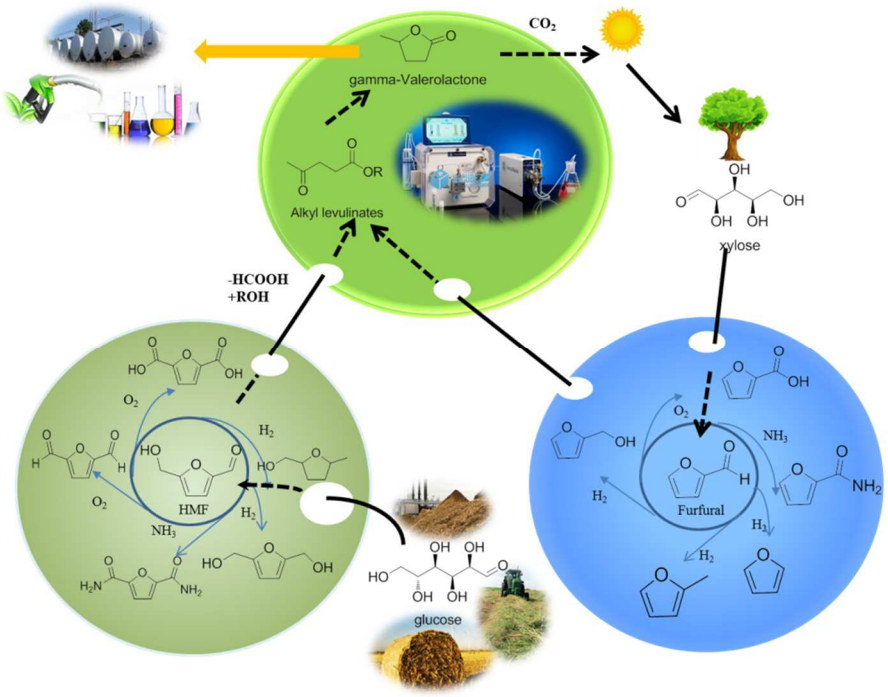
stability under optimum condition. The yield of GVL obtained from ethyl levulinate, butanol levuliante and levulinate acid were *ca.*21%, 54% and 26% less than ML in 2-PrOH and Pr were 0.43, 0.73 and 0.48 less respectively. There is no obvious hydrogenation process when changed 2-PrOH to ethanol and 1-butanol.

Keywords: Continuous flow, alkyl levulinates, γ-valerolactone，5%Ru/C

1. Introduction

The rapid developments in industry and transportation all over the world have led to a drastic increase in the demand for fuels. The gradual depletion of fossil fuel resources has stimulated the global efforts to search for alternative sources. Biomass is an abundant and renewable alternative resource that is the best candidate to replace fossil fuels for the sustainable production of energy [1-5], as well as chemicals [6-11]. The development of efficient processes to convert biomass resource into liquid fuels and valuable chemicals is a key research area in the next few decades [12-19]. Recent advances in the field of catalytic valorization of lignocellulose for the sustainable production of bulk chemicals and fuel additives have been reported [20]. γ-Valerolactone (GVL) as one of the most appealing molecules shows a very promising versatile intermediate for production of fuel additives, a renewable solvent, food ingredient, liquid fuel, and ideal precursor for the production of more valuable chemicals [21,22] in a wide range of applications (e.g., cutting oils and brake fluids) [23]. Due to very high interest towards GVL, its efficient production is currently a topic of intensive research.

The production of GVL from biomass has received extensive research interests. Starting from cellulose and hemicellulose [19], successive hydrolysis, dehydration/rehydration and then hydrogenation furnished GVL. The use of intermediates such as carbohydrate [24, 25], 5-hydroxymethylfurfural and furfuryl alcohol (FA) [26] was also developed efficiently for the production of GVL (Scheme 1). The hydrogenation of levulinic acid (LA) to GVL using heterogeneous and homogeneous catalysts in combination with molecular hydrogen has been studied extensively [27,28]. Unfortunately, the synthesis of LA in acidic aqueous media has got some drawbacks: production of a large amount of waste, a high cost for mineral acid recovery, humin formation and a rather difficult separation of the highly polar molecule LA [29, 30]. Comparatively, the hydrogenation of alkyl levulinates (AL) to GVL is more attractive because AL was obtained in better yield with a more efficient separation process. Thus, it is meaningful to establish a new integrated route to produce GVL from hemicellulose *via* successive formation of xylose, furfural, FA and AL.



Scheme 1. Production of biomass-derived GVL from cellulose (in green) and hemicellulose (in blue) *via* AL as a common intermediate.

Molecular hydrogen (H_2) is widely used as the reductant for catalytic transformation of LA or AL to GVL whether in batch or continuous flow [27, 28, 31]. Recently, heterogeneous catalytic transfer hydrogenation (CTH) of bio-based compound in the presence of hydrogen donors (e.g. 2-PrOH) has emerged [32]. CTH is more attractive for techno-economic point of view but also because the interphase transfer is improved (solid/liquid for ROH *vs.* solid/liquid/gas for H_2). Furthermore it offers a simple, efficient and safe option for the valorization of biomass derived molecules using abundant and inexpensive alcohols as hydrogen source and solvent as compared to H_2 [33-35]. Various metal catalysts have been demonstrated to have good activities for the conversion of AL and LA to GVL using CTH process. Kobayashi et al. reported a CTH process for the conversion of cellulose to sugar

alcohols over supported Ru/C as the catalyst and 2-PrOH as the hydrogen donor [36]. Batch microwave-assisted hydrogenation as alternative technology was studied for the conversion of LA and AL to GVL through catalysts screening experiments (Pt/C, Pd/C, Rh/C, Cu/C, Ni/C and Ru/C) and ruthenium exhibited the highest activity [37]. Heterogeneous Zr-based catalysts, such as ZrO_2 [38], hydrated zirconia ($ZrO(OH)_2 \cdot xH_2O$) [39] and Zr-beta [40] having amphoteric nature permitted to produce GVL in good productivity.

Continuous flow chemistry as alternative technology offers significant processing advantages including improved thermal management, mixing control, application to a wider range of reaction conditions, scalability, energy efficiency, waste reduction, safety, use of heterogeneous catalysis, multistep synthesis and much more [41-55]. In the context to develop new green process, few works on the production of GVL in continuous flow have been reported [31, 42]. Starting from LA, the use of heterogeneous 5% Ru/C in the presence of sulfonated phosphine as ligand and hydrogen under 10 bar at 140 °C permitted the production of GVL in continuous flow with a high productivity (0.8 mol g^{-1} h^{-1}) [31]. In parallel, our group described a high GVL productivity *via* CTH with Zr-based catalyst (0.0923 mol g^{-1} h^{-1}) starting from methyl levulinate (ML) in the presence of functional metal organic framework at elevated temperature (240°C) in continuous flow [42]. To date, an outstanding of the continuous flow catalytic transfer hydrogen process to produce GVL from AL is requested. In this context, the present work tested some commercial catalyst: 5%Ru/C, 5%Pd/C, 10%Pt/C and 5% Ru/Al_2O_3 for a continuous flow conversion of biosourced

ML to GVL using CTH process.

2. Materials and methods

2.1. Materials

Methanol (MeOH, ≥ 99.9%), propan-1-ol (1-PrOH, ≥ 99.5%), propan-2-ol (*2*-PrOH, ≥ 99.5%), ML (99%), GVL (99 %) and *n*-decane (≥ 99%) were purchased from Sigma-Aldrich and further used without purification. ML feedstocks of 0.2, 0.4 and 0.8 M were prepared by dissolving 2.602 g, 5.204 g and 10.40 g ML in propan-2-ol (100 mL) in a volumetric flask using *n*-decane (5.0mg/mL) as external standard. The commercial 5%Ru/C, 5%Pd/C, 10%Pt/C and 5% Ru/Al_2O_3 were purchased from Sigma-Aldrich and further used without purification.

2.2. General procedure for the synthesis of GVL in continuous flow experiment

The experiments were carried out in a high-temperature high-pressure H-Cube Pro™ Flow Reactor ThalesNano™, Hungary (Figure S1), connected to a HPLC pump to supply a continuous feed of ML (0.2-0.8 M) in *2*-PrOH，MeOH or 1-PrOH. A 70 mm CatCart cartridge (0.88 mL empty volume) was packed with 330 mg catalyst by applying vacuum suction at the bottom of the cartridge. The total flow through volume (including feed, reactor and product sections) was 6 mL. First, pure *2*-PrOH, MeOH or 1-PrOH was pumped through the system and then the feed was changed to the ML feedstock. The flow was continued until the temperature (100-150 °C) and hydrodynamic pressurization (0-50 bar) of the reactor module were reached. Then, in function of the flow rate (0.2-0.8 mL min^{-1}), the reaction proceeded during a certain

time (12-50 min) before collecting the first sample (time zero). Further samples were collected after regular time intervals.

Identical procedure was done starting from ethyl levulinate (EL) and butyl levulinate (BL).

2.2. Product analysis

GC-FID analysis was performed on a gas chromatograph (HP, 14009 Arcade, New York, United States) coupled with a FID detector equipped with a Supelco 2-8047-U capillary column (15 m x 0.25 mm i.d. and 0.25 μm film thickness, Alltech Part No.31163-01). H_2 was used as carrier gas at 1 mL min^{-1} flow rate. The samples were injected directly onto the column using septum-equipped programmable injector (SPI) system. The temperature of the injector was set 250 °C and the oven started at 70 °C, held for 1 min, raised to 250 °C at a rate of 20 °C min^{-1}, held for 10 min. The ionization mode was FID (70 eV, 300 μA, 250 °C). The identification of the compounds was performed by comparison of the retention times with pure standards and by GC/MS analysis. The solvent delay time was 0.90 min. The retention times of GVL, ML, EL, BL, methyl 4-hydroxypentanoate (MHP), ethyl 4-hydroxypentanoate (EHP), butanol 4-hydroxypentanoate (BHP) and LA, n-decane were 3.58 min, 3.39 min, 3.92 min, 5.21 min, 3.69 min, 4.16 min, 5.44 min, 4.98 min, 2.30 min. respectively. The response factors (RF) of ML and GVL relative to a fixed concentration (5.0 mg/mL) of *n*-decane as internal standard were experimentally determined at 3.62 and 3.01, respectively. The linear regression coefficients of the

calibrations were high in all cases ($r^2 > 0.99$). The RF for MHP, EHP and BHP were calculated according to the Effective Carbon Number (ECN) method [56], based on the RF and ECN factor of ML (3.75), EL (4.75), BL (6.75) and the ECN factor of MHP (4), EHP (5), BHP (7).

Mass spectra were record on a Hewlett-Packart HP 5973 mass spectrometer *via* a GC/MS coupling with a Hewlett-Packart HP 6890 chromatograph equipped with a capillary column HP-5MS (50 m x 0.25 mm i.d. and 0.25 µm film thickness, Alltech Part No.31163-01). lonisation was performed by electronic impact (EL, 70 eV). Mass spectra are reported as m/z (% of relative intensity).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker AC 300 (300 MHz) or a Bruker AC 400 (400 MHz). The chemical shifts are expressed in parts per million (ppm) referenced to residual chloroform (7.26 ppm). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a Bruker AC 300 (75 MHz) or a Bruker AC 400 (100 MHz). The chemical shifts are expressed in parts per million (ppm) relative to the centre line of the triplet at 77.16 ppm for $CDCl_3$

The yield and conversion in continuous flow were calculated according to eqs. (1) - (2):

(1) $$Yield\ (\%) = \frac{CP_{Product}}{CML_{Feed}} \times 100\ \ (Continuous\ \ flow)$$

(2) $$Conversion\ (\%) = \frac{[CML_{Initial} - CML_{Final}]}{CML_{Initial}} \times 100\ \ (Continuous\ \ flow)$$

CML and CP are the concentrations of ML and product (mol/mL). The total volume in the system of the continuous flow experiments was assumed to remain constant during the experiments (no evaporation loss). All results (conversion and yield) are expressed as molar percentages. The metal-based catalyst productivity ($mol(GVL)\ g(metal)^{-1}h^{-1}$) was calculated using eq. (3):

(3 $Productivity\ (mol\ g^{-1}h^{-1})$

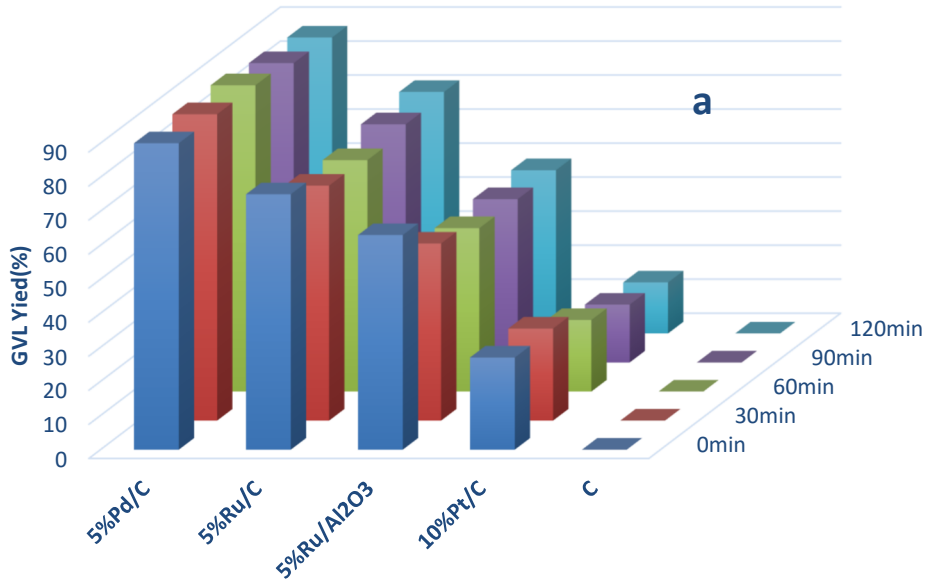
) $= \frac{[Flow\ rate\ (mL\ min^{-1})\ \times\ 0.06\ \times\ ML\ concentration\ (M)\ \times Y\ ied(}{Catalyst\ metal\ mass\ (g)}$

3. Results and discussion

3.1. Catalyst activity screening experiments

Continuous flow chemistry generally offers a better control and allows a higher flexibility in reaction conditions, which typically require optimization to improve the conversion and selectivity. 2-PrOH has been reported as an active hydrogen donor, which could provide good conversion and product selectivity when compared with other primary alcohols such as methanol, ethanol, 1-propanol [57, 58]. Thus, 2-PrOH was selected as hydrogen donor for CTH of ML under continuous flow conditions. Starting from ML (0.2 M) in 2-PrOH at 130 °C, four commercial catalysts 5%Pd/C, 5%Ru/C, 5%Ru/Al_2O_3 and 10%Pt/C were tested for the two successive steps: hydrogenation and lactonization aiming to reach high GVL yields (Fig. 1). The blank experiment (activated carbon as catalyst) did not give any ML conversion whatever the residence time (0-120 min). However, when the tested noble metals were

supported on activated carbon GVL was obtained in moderate to good yield. In our hands, the highest GVL yield (89%) was achieved in the presence of 5%Pd/C with 10% higher than that with 5% Ru/C. Nevertheless, 5% Ru/C was used for the next step of our optimization since this catalyst permitted to have the highest GVL productivity (0.2 mol g^{-1} h^{-1}). This result was in accordance with that reported in the literature [59].



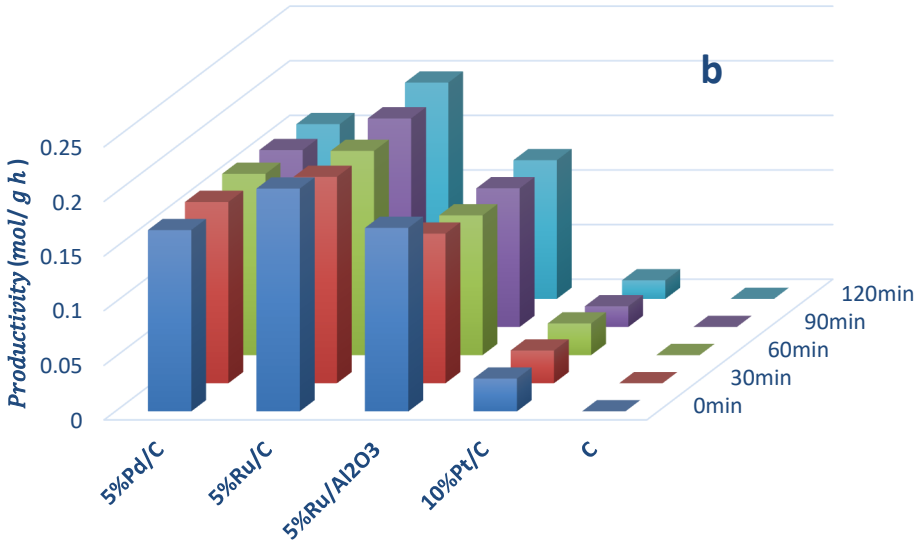


Fig. 1. Effect of catalysts and residence time on (a) the GVL yields and (b) on the productivity. Reaction conditions: ML (0.2 M), catalyst (0.88 cm^3 of the CatCart cartridge), 2-PrOH, 130 °C, 20 bar, 0.4 mL min^{-1}.

3.2. Effect of reaction temperature for the production of GVL

In a first step, the effect of reaction temperature (100-150 °C) was studied using ML (0.2 M) at 20 bar in a continuous flow system (0.4 mL min^{-1}) (Fig. 2). Whatever the temperature, ML furnished two main compounds: GVL and MHP (Fig. S2) and unidentified side compounds with a full conversion. With the increase of reaction temperature from 100 °C to 150 °C, the GVL yield and productivity (Pr) increase from 30% to 85% yield and from 0.084% to 0.254%, respectively. It was obvious that the MHP yield decrease from 60% to 8% with the increase of temperature because the lactonization of MHP to GVL was favored at higher temperature [60]. Whatever the

temperature used, the amount of side products was almost similar (3%). Among them, isopropyl 4-hydroxypentanoate obtained by transesterification between ML and 2-PrOH was identified (Fig. S3). Besides, the 5%Ru/C catalyst showed an excellent catalytic stability at the temperatures investigated. Due to the maximum temperature limitation of H-Cube Pro^{TM} Flow Reactor, higher reaction temperature than 150ºC was not available.

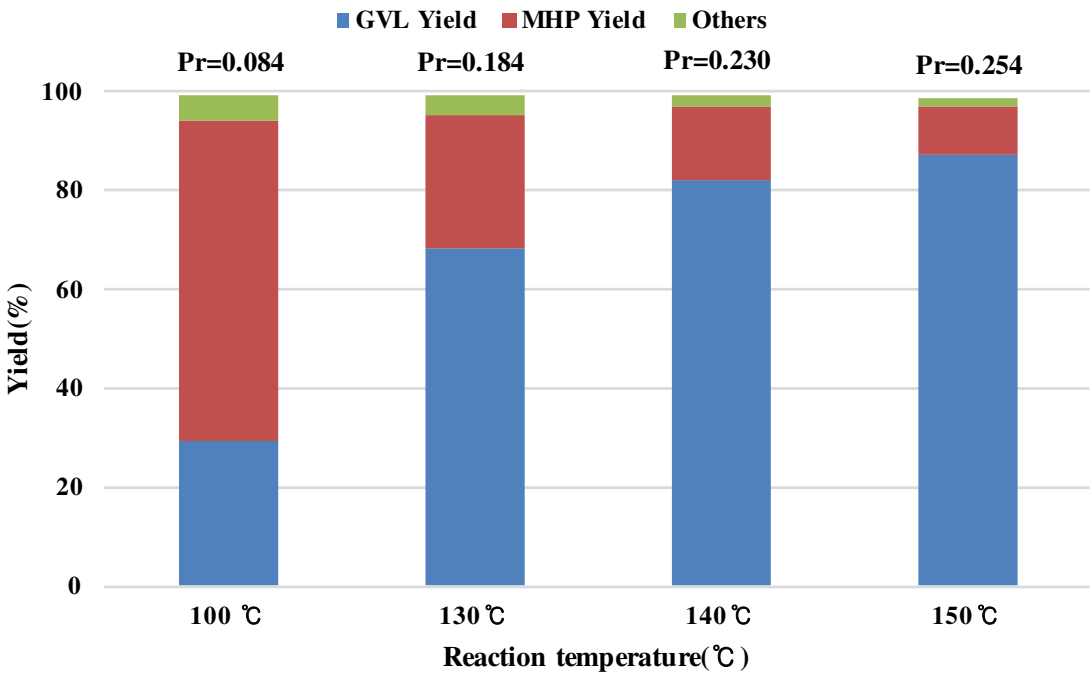


Fig. 2. Effect of reaction temperature on GVL productivity and products yield in continuous flow process. Reaction conditions: ML (0.2 M), 5% Ru/C (330 mg), 2-PrOH, 20 bar, 0.4 mL min^{-1}.

3.3. Effect of reaction pressure for the production of GVL

The effect of hydrodynamic pressure (20, 40, 60 bar) at 150 °C was also investigated for 120 min, which corresponded to the processing capacity 58 mL (120

min x 0.4 mL min^{-1} + 10 mL) in continuous flow (Fig. 3). Whatever the pressure used, full conversion of ML was obtained. The yield of GVL was improved *ca*. 7% with the increase of reaction pressure from 20 bar to 40 bar and the yield of MHP decreased 5%. With a higher pressure (60 bar *vs* 40 bar), no apparently changes of GVL and MHP yields were observed. From the point of energy conservation, the pressurization was set as 40 bar for the following optimization reactions.

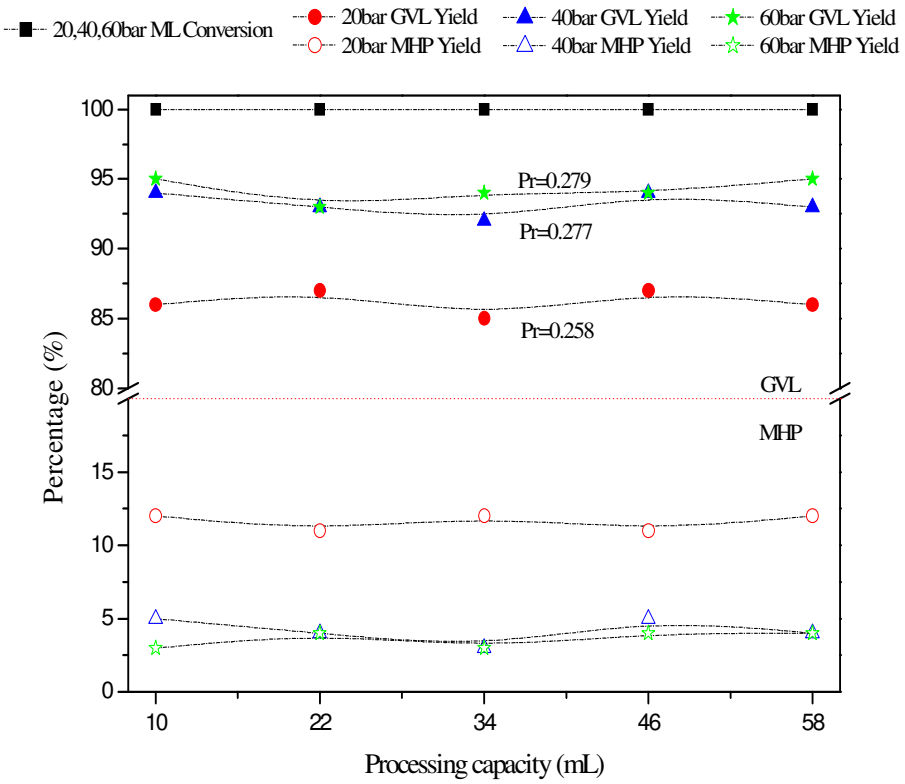


Fig. 3. Effect of hydrodynamic pressure on GVL productivity and products yield and productivity in continuous flow process. Reaction conditions: ML (0.2 M), 5% Ru/C (330 mg), 2-PrOH, 150 °C, 20-60 bar, 0.4 mL min^{-1}.

3.4. Effect of flow rate for the production of GVL

The effect of flow rate (0.2, 0.4 and 0.8 mL min^{-1}) on GVL and MHP yields at 150 °C and 40 bar in the presence of 5%Ru/C was studied and compared at different processing capacity (10 mL to 58 mL) (Fig. 4). Whatever the flow rate used, ML was fully converted. With a low flow rate (0.2 mL min^{-1}), the highest GVL yield was achieved (95% yield) with only 5% MHP. As expected, the decrease of residence time implying by the increase of the flow rate afforded a lower GVL yield (87-92% *vs* 95%) and a higher MHP yield (6-8% *vs* 2%). It was obvious that a lower flow rate offered a longer residence time, which favored the reactant contact with the Ru catalyst. In term of productivity, a short residence time with 0.8 mL min^{-1} flow rate gave a better result compared with a long residence time obtained with 0.2 mL min^{-1} flow rate (0.551 *vs* 0.131). Nevertheless, the presence of MHP as side product was a limiting step of the process and required more energy for the work-up and purification. Therefore, the flow rate of 0.2 mL min^{-1} with only 2-3 % of MHP was choose for the next step of the optimization.

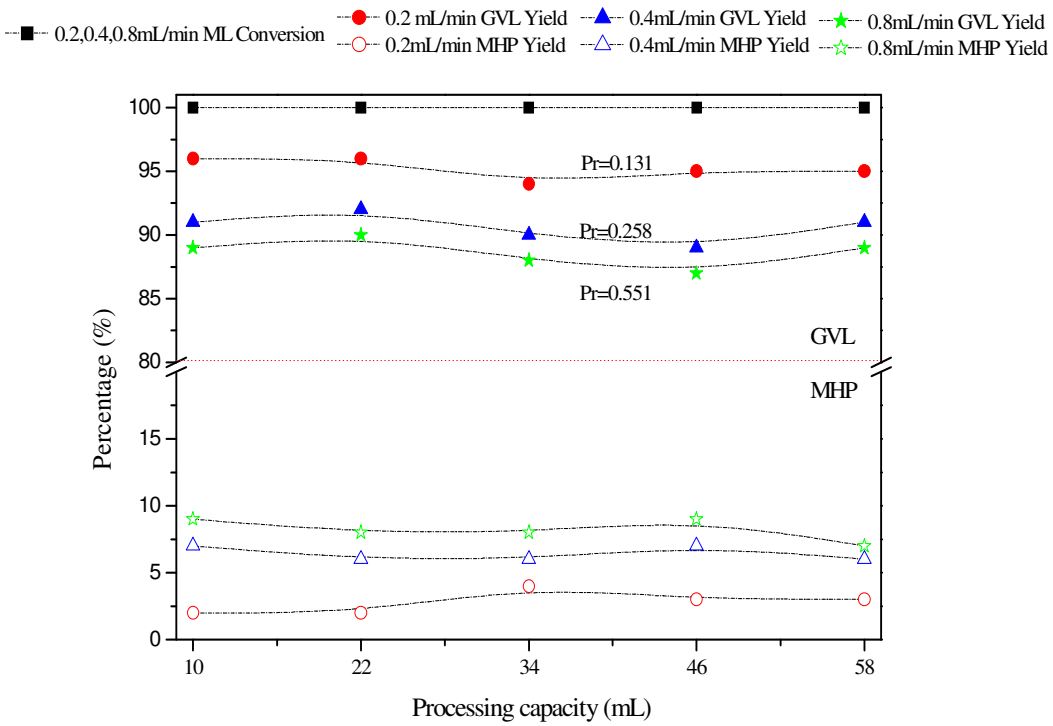


Fig. 4. Effect of flow rate on GVL productivity and products yield in continuous flow process. Reaction conditions: ML (0.2 M), 5% Ru/C (330 mg), 2-PrOH, 150 °C, 40 bar, 0.2-0.8 mL min^{-1}.

3.5. Effect of the concentration of ML for the production of GVL

With the perspectives to obtain a higher productivity and to have a solvent economy, variation of ML concentration was studied. In the present work, ML feeding rate was kept constant (0.16 mmol min^{-1}) and ML concentration was increased while flow rate was decreased (Fig. 5). Although the ML feeding rate was constant the conversion of ML, yields of GVL and MHP were different between 0.2 mL min^{-1} and 0.4-0.8 mL min^{-1}. With a low flow rate (0.2 mL min^{-1}), the conversion

of ML was lower than that obtained with a flow rate of 0.4-0.8 mL min^{-1} (90% *vs* 100%). Similar observations were observed with the GVL yields (80% *vs* 87-90%) and the MHP yields (6% *vs* 9%). Whatever the flow rate, these experiments showed that the target GVL and the acyclic MHP were obtained as the main chemicals and as the minor chemicals, respectively. The best results obtained using 0.8 mL min^{-1} and ML (0.2 M) can be explained by a short residence time and low concentration of starting material. The reactant adsorption on catalyst surface as well as the desorption of the target product were more efficient and favor high mass transfer rate. With ML concentration (0.2 M and 0.4 M), almost the same GVL productivity (*ca.* 0.55) because similar ML conversion and GVL yield were achieved. From the point of saving solvent, higher feedstock concentration could be a better choice. ML feeding rate was increased to 0.32 mmol min^{-1} (ML 0.4 M and flow rate 0.8 mL min^{-1}). The conversion of ML (98%) and the yield of GVL (85%) with *ca.*11% MHP yield were obtained and the productivity (0.99 mol g^{-1} h^{-1}) was remarkably superior to several systems in previous report (Table 1).

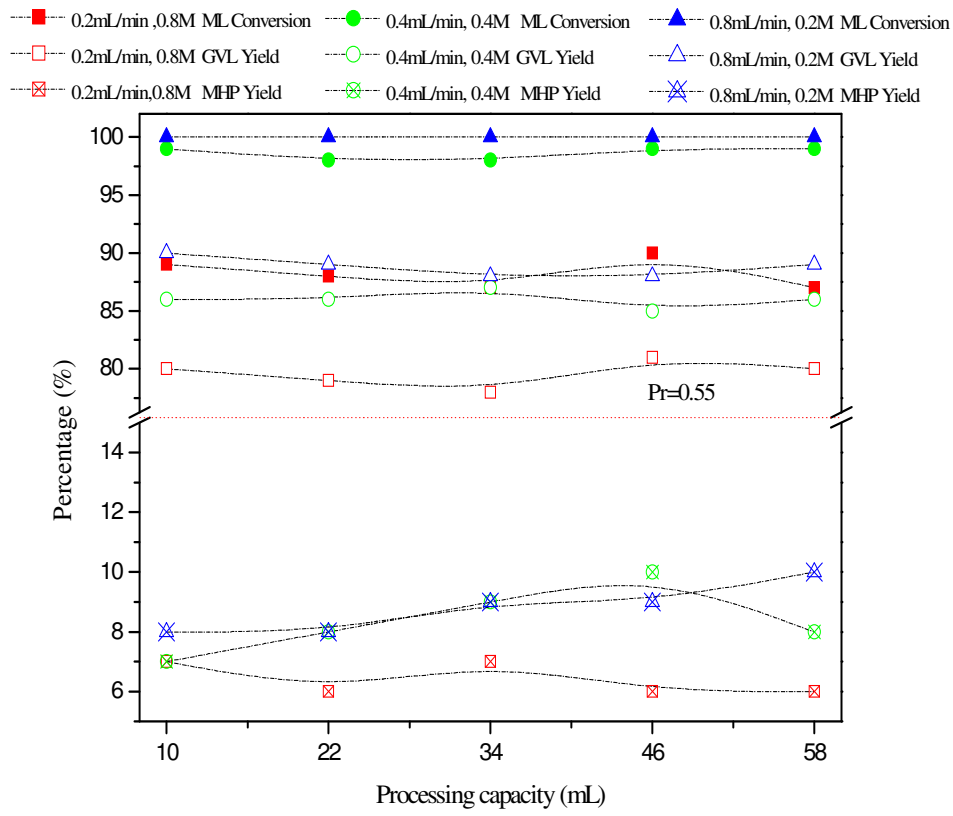


Fig. 5. Effect of flow rate and substrate concentration with a constant ML feeding rate on GVL and MHP yields in continuous flow process. Reaction conditions: ML (0.2-0.8 M), 5% Ru/C (330 mg), 2-PrOH, 150 °C, 40 bar, 0.2-0.8 mL min^{-1}.

Selected works describing the production of GVL from LA or AL in the presence of hydrogen source and 5% Ru/C as catalyst in either batch reactor with or without microwave radiation or continuous flow reactor were described (Table 1). CTH using formic acid and 2-PrOH gave not good productivity even the yield of GVL can reach 93% yield (Table 1, entries 1 and 2). It was noteworthy that the use of high concentrated solution of ML (1.4 M *vs* 0.43 M) and higher pressure of H_2 (30 bar *vs* 12 bar) permitted to have a better productivity (2.25 mol g^{-1} h^{-1} *vs* 1.12 mol g^{-1} h^{-1})

(Table 1, entries 3 and 4). Due to practical considerations, microwave-assisted hydrogenation of LA and AL was studied in batch reactor and not in continuous flow reactor. In this context, the use of 2-PrOH and LA as well as ML permitted to produce GVL with a good productivity (> 2 mol g^{-1} h^{-1}) (Table 1, entries 5 and 6). Unfortunately, when the alkyl chain was higher than one carbon atom the productivity decreased drastically (Table 1, entries 7 and 8). Starting from LA in the presence of 2-BuOH the microwave-assisted organic synthesis did not furnished GVL with good yield but the productivity was significant (1.92 mol g^{-1} h^{-1}) (Table 1, entry 9). In accordance with literature, microwave-assisted reaction permitted to have a short reaction time (30 minutes). The main problem of this process was the formation of side compounds, which limit their further utilization. For continuous flow as alternative technology, the production of GVL was studied using hydrogenation and CTH processes. Whatever the pressure used, LA furnished GVL in good to excellent yields with a productivity lower than 0.9 mol g^{-1} h^{-1} (Table 1, entries 10-12). Starting from AL such as BL in the presence of primary alcohol (1-BuOH) as hydrogen donor, the productivity decreased ten times (0.085 mol g^{-1} h^{-1} *vs* 0.832 mol g^{-1} h^{-1}) (table 1, entry 13). Our optimized process (ML (0.4 M), 5%Ru/C (330 mg), 2-PrOH, 150 °C, 40 bar, 0.8 mL min^{-1}) furnished the target lactone in 83% yield with a productivity of 0.99 mol g^{-1} h^{-1}, which is the best reported in the literature for a continuous flow process.

Table 1

5%Ru/C as catalysts reported for the conversion of LA and AL to GVL.

Entry	Starting material (M)	H source	Temperature (° C)	Time (h)	Yield of GVL (%)	Productivity of GVL (mol g^{-1} h^{-1})	Ref
1 [a]	LA (2 M)	Formic acid	150	5	21	0.084	[61]
2 [a]	EL (7.8 M)	2-PrOH	80	9	93	0.31	[35]
3 [a]	ML (0.43 M)	H_2 (12 bar)	130	2.7	87	1.120	[62]
4 [a]	ML (1.4 M)	H_2 (30 bar)	120	5	82	2.250	[60]
5 [b]	LA (0.43 M)	2-PrOH	140	0.5	41	2.820	[37]
6 [b]	ML (0.43M)	2-PrOH	140	0.5	34	2.330	[37]
7 [b]	EL (0.43M)	2-PrOH	140	0.5	6	0.412	[37]
8 [b]	BL (0.43 M)	2-PrOH	140	0.5	2.4	0.165	[37]
9 [b]	LA (0.43 M)	2-BuOH	140	0.5	28	1.926	[37]

10 [c]	LA (0.1 M)	H_2 (10 bar)	140	0.38 [d]	97	0.832	[31]
11 [c]	LA (0.1 M)	H_2 (50 bar)	100	0.38 [d]	68	0.582	[31]
12 [c]	LA (0.1 M)	H_2 (100 bar)	100	0.38 [d]	83	0.710	[31]
13 [c]	BL (1.0 M)	1-BuOH	150	4[d]	81	0.085	[63]
14 [c]	ML (0.4 M)	2-PrOH	150	1.1 [d]	83	0.990	this work

[a] conventional heating in batch reactor.

[b] microwave-assisted reaction (300 W) in batch reactor.

[c] conventional heating in continuous flow reactor.

[d] residence time/min.

3.6. Effect of the nature of the alkyl levulinate (AL) for the production of GVL

Among the different results obtained with 5% Ru/C as catalyst, our optimized conditions (ML (0.4 M), 5% Ru/C, 2-PrOH, 150 °C, 40 bar, 0.8 mL min^{-1}) was selected and variation of the nature of the alcohol was investigated (Table 2). With the increase of carbon atoms (from C1 to C4) (Table 2, entries 1-3), the yield of GVL decreased from 85% to 31% while the intermediate AHP yield increased from 13% to 63%. As a consequence, the productivity decreased from 0.99 to 0.25 mol g^{-1} h^{-1}. In accordance with the literature, the subsequent reduction of the ketone to the corresponding alcohol and the lactonization were facilitated with an AL having a little molecular weight [60]. When the carboxylic acid LA was used as starting material, GVL was obtained in 59% with a low conversion (67%) but the productivity was similar to that starting from EL (ca. 0.5 mol g^{-1} h^{-1}) (Table 2, entry 4).

Table 2

Effect of AL molecular weight as starting material for the production of GVL.[a]

Entry	AL	Conversion (%)	GVL yield (%)	AHP yield (%)[b]	Productivity (mol g^{-1} h^{-1})
1	ML	99	85	13	0.99
2	EL	95	64	31	0.55
3	BL	94	31	63	0.25
4	LA	67	59	6[c]	0.50

[a] Reaction conditions: ML (0.4 M), 5% Ru/C (330 mg), 2-PrOH, 150 °C, 40 bar, 0.8 mL min^{-1}.

[b] AHP for alkyl 4-hydroxypentanoate.

[c] 4-hydroxypentanoic acid.

3.7. Stability of the catalyst for the production of GVL

Further catalyst stability experiments were performed using our optimized conditions. The conversion remained stable over 9 hours at least, the yields of GVL and MHP were *ca.*83% and 10 %, respectively (Fig. 6). In our lab-scale process, the stability of 5% Ru/C catalyst was good.

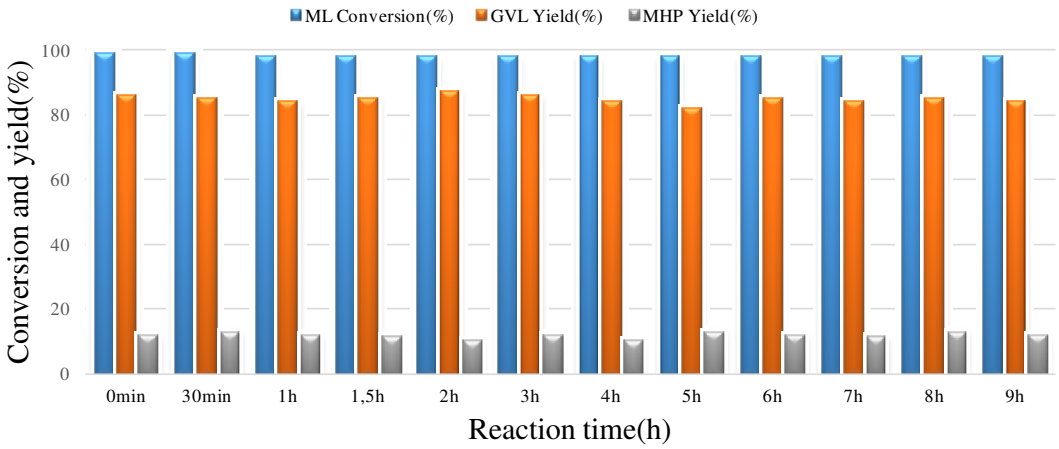


Fig. 6. Operational stability of the catalyst 5% Ru/C in continuous flow alcoholysis of ML. Reaction conditions: ML (0.4 M), 5% Ru/C (330 mg), 2-PrOH, 150 °C, 40 bar, 0.8 mL min^{-1}.

4. Conclusion

This works reports a new efficient process using commercial heterogeneous catalyst 5% Ru/C for the production of γ-valerolactone (GVL) in continuous flow from either levulinic acid (LA) or alkyl levulinates (AL). After the investigation of methyl levulinate (ML) experiment parameters (reaction temperature, pressure, flow rate, starting material concentration), the optimization condition was at ML (0.4 M) in 2-PrOH, 5% Ru/C(330mg), 150 °C, 40 bar, flow rate=0.8 mL min^{-1}. Feedstock were fully converted with 85% GVL yield, and 13% methyl 4-hydroxypentanoate (MHP) yield, with the highest productivity is 0.99 mol g^{-1} h^{-1}. Effect of the nature of the AL experiments showed the lactonization were facilitated with shorter AL alkyl chains. Finally 5%Ru/C shows good stability in 9 h cycle experiments.

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Appendix A. Supplementary data

The Supporting Information is available:

References

[1] J.C. Escobar, E.S. Lora, O.J. Venturini, E.E. Yáñez, E.F. Castillo, O. Almazan, Renewable and sustainable energy reviews 13 (2009) 1275-1287.

[2] D.M. Alonso, J.Q. Bond, J.A. Dumesic, Green Chem. 12 (2010) 1493-1513.

[3] P.S. Nigam, A. Singh, A. Progress in energy and combustion science 37 (2011) 52-68.

[4] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Green Chem. 15 (2013) 584-595.

[5] G.W. Hber, S. Iborra, A. Corma, A. Chem. Rev. 106 (2006) 4044-4098.

[6] A. Corma, S. Iborra, S., A. Velty, A. Chem. Rev. 107 (2007) 2411-2502.

[7] P. Gallezot, Chem. Soc. Rev. 41 (2012) 1538-1558.

[8] A. Takagaki, S. Nishimura, K. Ebitani, K. Catal. Surv. Asia 16 (2012) 164-182.

[9] J. Zhang, S. Wu, B. Li, H. Zhang, ChemCatChem 4 (2012) 1230-1237.

[10] F. Delbecq, Y. Wang, A. Muralidhara, K. El Ouardi, G. Marlair, C. Len, Front. Chem. 6 (2018) 146.

[11] F. Delbecq, C. Len, *Molecules* 23 (2018) 1973.

[12] C.H. Zhou, X. Xia, C.X. Lin, D.S. Tong, J. Beltramini, J. Chem. Soc. Rev. 40 (2011) 5588-5617.

[13] J. Song, H. Fan, J. Ma, H. Han, Green Chem. 15 (2013) 2619-2635.

[14] I. Delidovich, K. Leonhard, R. Palkovits, Energy Environ. Sci. 7 (2014) 2803-2830.

[15] I.T. Horváth, H. Mehdi, V. Fábos, L. Boda, L.T. Mika, 10 (2008) 238-242.

[16] W.R. Wright, R. Palkovits, 5 (2012) 1657-1667.

[17] B.L. Oser, S. Carson, M. Oser, M. Food Cosmet. Toxicol. 3 (1965) 563-569.

[18] H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L.T. Mika, I.T. Horváth, I. T. Top. Catal. 48 (2008) 49-54.

[19] D.M. Alonso, J.M.R. Gallo, M.A. Mellmer, S.G. Wettstein, J.A. Dumesic, Catal. Sci. Technol. 3 (2013) 927-931.

[20] Q. Zhang, F. Jerome, ChemSusChem 6 (2013) 2042-2044.

[21] A.M.R. Galletti, C. Antonetti, V. De Luise, M. Martinelli, Green Chem. 14 (2012) 688-694.

[22] F.M. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, Angew. Chem. Int. Ed. 49 (2010) 5510-5514.

[23] A.P. Dunlop, J.W. Madden, (1957). *U.S. Patent No. 2,786,852*. Washington, DC: U.S. Patent and Trademark Office.

[24] L. Qui, I.T. Horváth, ACS Catal. (2014) 2012, 2, 2247-2249

[25] L. Qi, Y.F. Mui, S.W. Lo, M.Y. Lui, G.R. Akien, I.T. Horváth, ACS Catal. 4 (2014) 1470-1477.

[26] A.M. Hengne, S.B. Kamble, C.V. Rode, Green Chem. 15 (2013) 2540-2547.

[27] A.S. Piskun, J. Ftouni, Z. Tang, B.M. Weckhuysen, P.C.A. Bruijnincx, H.J. Heeres, Appl. Catal., A. 549 (2018) 197-206.

[28] A.S. Piskun, J.E. de Haan, E. Wilbers, H.H. van de Bovenkamp, Z. Tang, H.J. Heeres, ACS Sustain. Chem. Eng. 4 (2016) 2939-2950.

[29] X. Zheng, X. Gu, Y. Ren, Z. Zhi, X. Lu, BioFPR 10 (2016) 917-931.

[30] F.D. Pileidis, M.M. Titirici, ChemSusChem 9 (2016) 562-582.

[31] J.M. Tukacs, R.V. Jones, F. Darvas, G. Dibó, G. Lezsák, L.T. Mika, RSC Adv. 3 (2013) 16283-16287.

[32] G. Yi, Y. Zhang, ChemSusChem 5 (2012) 1383-1387.

[33] X. Tang, H. Chen, L. Hu, W. Hao, Y. Sun, X. Zeng, L. Lin, S. Liu, S. Appl. Catal., B. 147 (2014) 827-834.

[34] J. He, H. Li, Y.M. Lu, Y.X. Liu, Z.B. Wu, D.Y. Hu, S. Yang, Appl. Catal., A. 510 (2016) 11-19.

[35] Z. Yang, Y.B. Huang, Q.X. Guo, Y. Fu, Chem. Commun. 49 (2013) 5328-5330.

[36] H. Kobayashi, H. Matsuhashi, T. Komanoya, K. Hara, A. Fukuoka, Chem. Commun. 47 (2011) 2366-2368.

[37] M.G. Al-Shaal, M. Calin, I. Delidovich, R. Palkovits, Catal. Commun. 75 (2016) 65-68.

[38] M. Chia, J.A. Dumesic, Chem. Commun. 47 (2011) 12233-12235.

[39] X. Tang, L. Hu, Y. Sun, G. Zhao, W. Hao, L. Lin, RSC Adv. 3 (2013) 10277-10284.

[40] H. Li, Z. Fang, S. Yang, ACS Sustain. Chem. Eng. 4, (2016) 236-246.

[41] L. Vaccaro, D. Lanari, A. Marrocchi, G. Strappaveccia, Green Chem. 16 (2014) 3680-3704.

[42] W. Ouyang, D. Zhao, Y. Wang, A.M. Balu, C. Len, R. Luque, ACS Sustain. Chem. Eng. 6 (2018) 6746-6752.

[43] H. Yalgin, D. Luart, C. Len, J. Flow Chem. 6 (2016) 80-85.

[44] E. Banaszak-Leonard, F. Mangin, C. Len, New J. Chem. 40 (2016) 7414-7420.

[45] N. Sotto, C. Cazorla, C. Villette, M. Billamboz, C. Len, J. Org. Chem. 81 (2016) 11065-11071.

[46] C. Cazorla, M. Billamboz, H. Bricout, E. Monflier, C. Len, Eur. J. Org. Chem. 6 (2017) 1078-1085.

[47] J. Garcia-Olmo, A. Yepez, A. M. Balu, P. Prinsen, A. Garcia, A. Mazière, C. Len, R. Luque, Tetrahedron 73 (2017) 5599-5604.

[48] N. Galy, R. Nguyen, P. Blach, S. Sambou, D. Luart, C. Len, J. Ind. Eng. Chem. 51 (2017) 312-318.

[49] C. Len, S. Bruniaux, F. Delbecq, V.S. Parmar, Catalysts 7 (2017) 146-168.

[50] C. Len, F. Delbecq, C.C. Corpas, E.R. Ramos, Synthesis 50 (2018) 723-740.

[51] S. Bruniaux, D. Luart, C. Len, Synthesis 50 (2018) 1849-1856.

[52] Y. Wang, P. Prinsen, K.S. Triantafyllidis, S.A. Karakoulia, A. Yepez, C. Len, R. Luque, ChemCatChem 10 (2018) 3459-3468.

[53] Y. Wang, P. Prinsen, K.S. Triantafyllidis, S.A. Karakoulia, P.N. Trikalitis, A. Yepez, C. Len, R. Luque, ACS Sustainable Chem. Eng. 6 (2018) 9831-9844.

[54] D. Zhao, P. Prinsen, Y. Wang, W. Ouyang, F. Delbecq, C. Len, R. Luque, ACS Sustainable Chem. Eng. 6 (2018) 6901-6909.

[55] R. S. Varma, C. Len, Curr. Opin. Green Sustain. Chem. 15 (2019) 83-90.

[56] R.L. Grob, E.F. Barry, (Eds.). (2004). Modern practice of gas chromatography. John Wiley & Sons,Inc.,2004.

[57] Y. Kuwahara, W. Kaburagi, T. Fujitani, RSC Adv. 4 (2014) 45848-45855.

[58] H.Y. Luo, D.F. Consoli, W.R. Gunther, Y. Román-Leshkov, J. Catal. 320 (2014) 198-207.

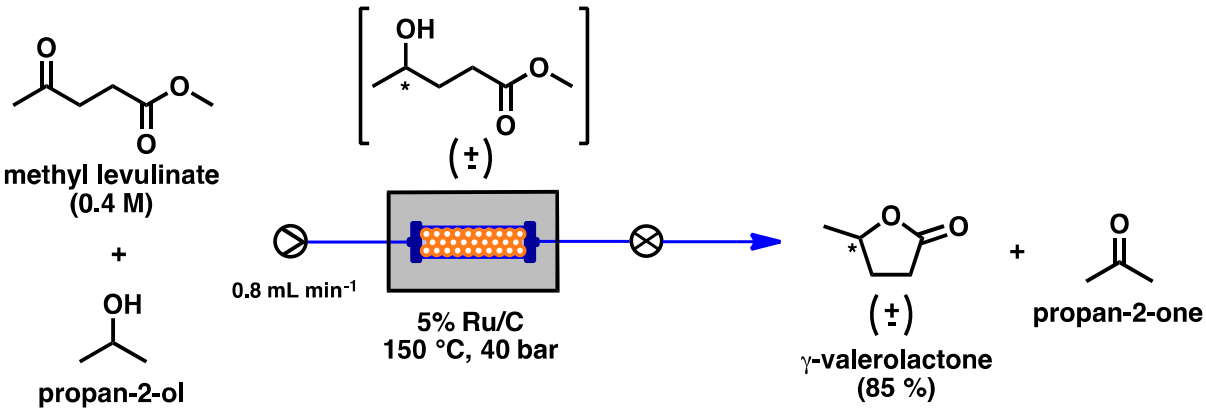
[59] C. Ortiz-Cervantes, J.J. García, Inorg. Chim. Acta 397 (2013) 124-128.

[60] L. Negahdar, M.G. Al-Shaal, F.J. Holzhäuser, R. Palkovits, Chem. Eng. Sci. 158 (2017) 545-551.

[61] P.A. Son, S. Nishimura, K. Ebitani, RSC Adv. 4 (2014) 10525-10530.

[62] M.G. Al-Shaal, W.R. Wright, R. Palkovits, Green Chem. 14 (2012) 1260-1263.

[63] E.I. Gürbüz, D.M. Alonso, J.Q. Bond, J.A. Dumesic, ChemSusChem 4 (2011) 357-361.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OH
(±)
0.8 mL min-1
5% Ru/C
150 °C, 40 bar
γ-valerolactone
(85 %)
+
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