Continuous flow alcoholysis of furfuryl alcohol to alkyl levulinates and angelica lactones using zeolites

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ABSTRACT: The present work explores the catalytic activity of various zeolites for the production of methyl levulinates from hemicellulose derived furfuryl alcohol and explores the performance of H-ZSM-5-50 in continuous flow alcoholysis. Good results were obtained with MFI zeolite H-ZSM-5-50, with methyl levulinate yields up to 80 % at 170 °C (50 bars) using a high load (1.6 M) feed at 0.2 mL min^{-1} flow rate. Angelica lactones were produced in significant amounts as one of the side products, albeit in lower amounts in continuous flow mode. Catalyst deactivation occurred at high furfuryl alcohol load through formation of pore blocking polyfurfuryl alcohols. The zeolites showed good re-usability after regeneration at 500 °C. The levulinates yields in ethanol and *n*-propanol were 20 % lower.

INTRODUCTION

Recent advances in the field of catalytic valorization of lignocellulose for the production of biofuels and chemicals aim to reach high yields of 1) hexitols through hydrogenation or 2) 5-hydroxymethylfurfural (HMF) through isomerization and dehydration of glucose or oligomers, produced from cellulose hydrolysis.[1,2] Similarly, furfural can be produced from xylose, as the major hydrolysis product from hemicelluloses.[3,4] Levulinic acid, as the 5-HMF hydrolysis product, is among the top target chemicals in lignocellulose biorefinery and it can be converted into various derivatives with several applications, particularly into alkyl levulinates as biofuel additive or precursor.[5] Alkyl levulinates can be obtained via esterification of levulinic acid with various alcohols.[6] Levulinic acid can be produced directly from various biomass sources in

acidic aqueous media, but this process deals with the production of waste, a high cost for mineral acid recovery, humin and char formation and a rather difficult separation of the highly polar molecule levulinic acid.[7,8] Some promising results were obtained using ionic liquids and with the carbohydrate derived solvent γ-valerolactone, and by using solid acid catalysts, like demonstrated recently for H-ZSM-5 in aqueous THF.[9] Alcoholysis is a promising alternative to tackle these problems and opens ways for direct conversion of sugar monomers,[10,11] like demonstrated very recently for methyl levulinate from glucose using sulfated zirconia.[12] Alcoholysis processes can also be employed starting from 5-HMF (**Scheme 1**, pathway displayed in green), without the need for isolation of levulinic acid from aqueous product streams. Likewise, alkyl levulinates can also be produced via selective hydrogenation of furfural to furfuryl alcohol (FA) followed by conversion in various alcohols (ROH), as illustrated in Scheme 1 (pathway displayed in blue). This conversion allows to increase the overall yield of a levulinate production plant from lignocellulose by converting a minor co-product, furfural or furfuryl alcohol, into its main product.

((Scheme 1))

Various solid acid catalysts have been demonstrated to work pretty fine for the conversion of FA to alkyl levulinates, as recently reviewed for ethyl levulinate by Haider and co-workers.[11] The alkyl levulinates yield increases with higher reaction temperature, higher catalyst dosage, longer reaction time and lower FA load. Considerable time laps were observed between FA conversion and the formation of alkyl levulinate, as multiple reaction intermediates are formed in

the alcoholysis.[13] A series of side products can be formed, originating from the reactants and

intermediates. One particular side product is polyfurfuryl alcohol, which may cause pore

blocking and occupation of the catalytic site. The formation of this oligomeric/polymeric side

product can be suppressed by operating at moderate temperatures and reducing the reaction time.

Most of the research studies on FA alcoholysis operated at temperatures between 110 and 140

°C,[4,14-18,20-22] with some exceptions.[19] Although strongly depending on the catalyst load and the

alcohol chain length, most of the studies required at least 2 h to attain full conversion and

typically 2-6 h to obtain high alkyl levulinates yields using 0.2-0.4 M feedstocks, with some

exceptions.[18,21] **Table 1** compares the activity of the most promising solid acid catalysts reported

for the conversion of FA to methyl-, ethyl- and butyl levulinate after 2 h reaction. Acidic ionic

liquids (Table 1, entries 3 and 11) are among the most efficient catalysts, but the environmental

impact resulting from their use today still remains not fully clear. Commercial catalysts such as

Amberlyst[TM] (entries 10 and 13) and α-Fe$_2$O$_3$ (entry 7) performed also well, although high

temperature is required when using α-Fe$_2$O$_3$. Catalysts decorated with sulfonic acid groups were

also reported in several occasions; SBA-15-SO$_3$H (entry 15) was found to be the best performing

one, at least when using 1-butanol. Various metal chloride salts, including AlCl$_3$ (entry 6), CuCl$_2$

(entry 14) but also FeCl$_3$, showed very promising results, although their recovery by filtration

may result costly or less efficient (metal leaching).[22] Sulfated zircona dioxide (entry 2) and

titanium dioxide are also catalyst candidates.[14]

((Table 1))

All the experiments reported in the literature on FA conversion to alkyl levulinates were performed in batch reactors. Haan and co-workers produced ethyl-levulinates in semi-batch mode as a strategy to overcome polyfurfuryl alcohol side product formation, by feeding the FA slowly to the batch reactor.[29] To the best of our knowledge, only one recent study reported the continuous flow alcoholysis of FA.[30] More research is required here, not only because of the already known advantages of continuous flow reactors such as better mass transfer, but also because it is likely that furfuryl alcohol feedstocks will be produced by selective continuous flow hydrogenation of furfural,[23-25] because furfural itself can be produced in relatively high yields in continuous flow[26-28] and because it may lower the formation of polyfurfuryl alcohol side products. The present study explores various zeolites for the conversion of FA to methyl levulinates and studies the behavior in continuous flow using a catalytic bed packed with the best performing zeolite. Alcoholysis in ethanol and propanol was also demonstrated.

EXPERIMENTAL SECTION

Materials, solvents and reagents. Furfuryl alchohol (FA, ≥ 98 %), methanol (MeOH, ≥ 99.9 %), ethanol (EtOH, ≥ 99.5 %), *n*-propanol (*n*-PrOH, ≥ 99.5 %), methyl levulinate (ML, 99 %), γ-valerolactone (GVL, 99 %) and *n*-decane (≥ 99 %) were purchased from Sigma-Aldrich and further used without purification. FA feedstocks of 0.1, 0.2, 0.4, 0.8 and 1.6 M were prepared by dissolving 0.993, 1.985, 3.979, 7.936 and 15.882 g FA in 100 mL alcohol in a volumetric flask using *n*-decane (5.0 mg mL^{-1}) as external standard. The commercial MFI zeolites CBV3024E and CBV5524G (H-ZSM-5-30 and H-ZSM-5-50 with SiO_2/Al_2O_3 molar ratios 30 and 50, respectively) and FAU zeolites CBV500 and CBV760 (H-Y-5.2 and H-Y-60 with molar SiO_2/Al_2O_3 ratios 5.2 and 60, respectively) were purchased from Zeolytes International (USA).

Catalyst synthesis and characterization. The commercial zeolite catalysts were calcined at 600 °C during 24 h prior to use in the catalytic experiments. The Fe/H-ZSM-5-50 catalyst was prepared mechanochemically in dry conditions: 1.0 g zeolite and 0.040 g FeCl$_2$.4H$_2$O (equivalent to 1.0 wt% Fe to reach a theoretical amount of 1.5 mol% Fe with respect to the FA load) were milled together in a planetary ball mill (Retsch 100) under optimized conditions (350 rpm, 10 min). The solids were recovered and heated under air atmosphere for 4 h at 400 °C. The Cu/H-ZSM-5-50 catalyst was prepared similarly using 0.03 g CuCl$_2$.2H$_2$O. Thermogravimetric (TGA) analysis was performed on a Perkin-Elmer thermal analyzer, by heating the sample up to 900 ºC at 10 ºC min.$^{-1}$ under dynamic air atmosphere (10 mL min.$^{-1}$). Powder X-ray diffraction patterns (XRD) were recorded on a Bruker D8-advance X-ray diffractometer with Cu Kα radiation (0.154 nm) over the 2Θ range of 10-80 º.

Batch alcoholysis experiments. The experiments were carried out in a closed pressure-controlled vessel under continuous stirring, assisted by microwave irradiation using a CEM-DISCOVER model with PC control, using 50 mg catalyst in 3 mL of a 0.2 M FA solution in MeOH. When reaching the set temperature (150 °C, 14 bars) after 1-2 min, time was set to zero and the reactions proceeded for 5 min. After the reaction, the mixture was cooled to room temperature (3 min) and filtered on 0.22 µm syringe filters. The filtrate was used for GC-FID analysis. All results (conversion and yield) are expressed as molar percentages.

Continuous flow alcoholysis experiments. The experiments were carried out in a high-temperature high-pressure Phoenix Flow Reactor (ThalesNano^{TM}, Hungary, see **Figure S1** in the Supporting Information), connected to a HPLC pump to supply a continuous feed of a 0.1-1.6 M FA solution in MeOH, EtOH or *n*-PrOH. A 70 mm CatCart cartridge (0.88 mL empty volume)

was packed with 200 mg catalyst and tightened in the reactor module. The total flow through volume (including feed, reactor and product sections) was 14 mL. First, pure MeOH, EtOH or *n*-PrOH was pumped through the system and then the feed was changed to the FA feedstock. The flow was continued until the temperature (90-190 °C) and hydrodynamic pressurization (0-50 bars) of the reactor module were reached. Then, in function of the flow rate (0.2-0.5 mL min^{-1}), the reaction proceeded during a certain time (12-30 min.) before collecting the first sample (sample at time = 0 min). Further samples were collected after regular time intervals. For recycle experiments, the catalysts were recovered by rinsing and washing with MeOH, centrifugation (4000 rpm, 10 min, 20 °C), drying at 100 °C and finally calcination at 500 or 800 °C, prior to re-utilization in the next experiment. All results (conversion and yield) are expressed as molar percentages.

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 (60 m x 25 m x 25 μm, Alltech Part No.31163-01). N$_2$ 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 80 °C, held for 5 min, raised to 100°C at a rate of 10 °C min^{-1}, held for 5 min and then raised to 120 °C at a rate of 10 °C min^{-1} and held for 10 min at 120 °C. 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 (see Supporting Information for experimental details). The solvent delay time was 3.00 min. The retention times of 2-methoxy-2-methylfuran (MMF), furfuryl alcohol (FA), 5-methyl-2(3H)-furanone (α-angelica lactone), FA, 5-methyl-2(5H)-furanone (β-angelica lactone, AL), methyl

levulinate (ML) and *n*-decane were 9.2, 9.8, 10.0, 11.7, 13.7 and 15.6 min, respectively. The response factors (RF) of FA, ML and γ-valerolactone (GVL) relative to a fixed concentration (5.0 mg mL^{-1}) of *n*-decane as internal standard were experimentally determined at 0.619, 0.415 and 0.549, respectively. The linear regression coefficients of the calibrations were high in all cases ($r^2 > 0.99$). The RF for angelica-lactones were calculated according to the Effective Carbon Number (ECN) method,[31] based on the RF and ECN factor of GVL (3.75) and the ECN factor of α/β-angelica lactone (3.65). Yield, conversion and selectivity (all in molar percentages) were determined as:

$$Yield\ (\%) = \frac{Mol_{Product}}{Mol_{Initial}} \times 100\ (Batch), Yield\ (\%) = \frac{CP_{Product}}{CFA_{Feed}} \times 100\ (Continuous\ flow)$$

$$Conversion\ (\%) = \frac{[Mol_{Initial} - Mol_{Final}]}{Mol_{Final}} \times 100\ (Batch), Conversion\ (\%) = \frac{[CFA_{Initial} - CFA_{Final}]}{CFA_{Initial}} \times 100\ (Continuous\ flow)$$

$$Selectivity\ (\%) = \frac{Mol_{Product}}{Conversion} \times 100\ (Batch\ and\ continuous\ flow)$$

CFA and CP are the concentrations of FA and alcoholysis product (mol mL^{-1}). The total volume in the system of the continuous flow experiments was assumed to remain constant during the experiments (no evaporation loss). The weight hourly space velocity (WHSV) was calculated as:

$$WHSV\ (g\ g^{-1}h^{-1}) = \frac{[Flow\ rate\ (mL\ min^{-1})\ \times 0.06\ \times FA\ concentration\ (M)\ \times 98.1\ (g\ mol^{-1})\ ]}{Catalyst\ mass\ (g)}$$

RESULTS AND DISCUSSION

Catalyst activity in batch alcoholysis experiments. Two commercial FAU zeolites (H-Y-5.2 and H-Y-60) and two commercial MFI zeolites (H-ZSM-5-30 and H-ZSM-5-50) were tested as solid acid catalysts for the alcoholysis of furfuryl alcohol (FA) feedstocks in methanol (MeOH),

aiming to reach high methyl levulinate (ML) yields. Whereas the blank experiment (no catalyst) resulted in 18 % conversion without any significant ML formation (< 0.5 %), conversions were near 100 % for all the zeolites with high ML yields after already 5 min (+ 2 min ramping time) microwave irradiation at 150 °C (**Figure 1**). Whereas reaction intermediates such as 2-methoxy-2-methylfuran (MMF), 5,5-dimethoxy-2-pentanone and others were only present in small amounts (6-13 %) for H-ZSM-5 zeolites, higher amounts (57-64 %) remained with the H-Y zeolites. The exact structure of the other reaction intermediates remained not fully clear from the GC/MS analysis, but their mass spectra clearly indicated structures equal or similar to those reported in the literature.[13,15] Although previously reported as a reaction intermediate,[15] in the present study angelica lactones were produced as side products. Their yield (33-34 %) was especially high when using H-ZSM-5 zeolites as the catalyst. According to the H-ZSM-5 catalytic activity reported by Xin et al.[32] and based on the mechanistic insights reported by Karwa et al.,[33] this side product arises via dehydration of levulinic acid to 5-hydroxy-γ-valerolactone which reacts further to α-angelica lactone (AAL), which can further isomerize to β-angelica lactone (BAL). Levulinic acid is no reaction intermediate, it is a side product resulting from the hydrolysis of levulinate within the acidic zeolite itself. Small amounts of water residues in the feed, adsorbed on the zeolite surface or formed as intermediate during the reaction itself can result in important changes in selectivity from levulinate to levulinic acid.[13,21] Very recently, angelica lactone isomers were reviewed as a biomass platform chemical and as high-value end-product in various food applications.[34] They are also naturally occurring compounds, particularly present in grapes, soybean, etc.

((Figure 1))

The main product, methyl levulinate (ML), was produced in yields between 54-60 and 30-37 %

for H-ZSM-5 and H-Y zeolites, respectively. This substantial difference between both type of

zeolites is mainly related to the lower acidity for H-Y as compared to H-ZSM-5 zeolites, as

recently reported by our research group.[35] Although H-ZSM-5-30 is slightly more acidic than H-

ZSM-5-50, 6 % lower ML yield was observed with the former catalyst. Other characteristics

such as specific surface area, pore volume and pore shape also may play a role. H-ZSM-5-50

exhibits higher total specific surface area than H-ZSM-5-30 (400 *vs.* 350 m^2 g^{-1}) and offers

higher external surface area (100 *vs.* 70 m^2 g^{-1}), which may explain this difference in ML yield.

Another important difference between both is that H-ZSM-5-30 is more disordered and contains

pores in the 24-40 nm range whereas H-ZSM-5-50 contains more micropores in the 2-5 nm

range. H-ZSM-5-50 is also more hydrophobic as it contains less Al and therefore it may adsorb

less water or exhibit better levulinate desorption. Anyhow, the H-ZSM-5-50 zeolite was the most

efficient catalyst for conversion into ML and this zeolite was used for further experiments. First,

it was modified by depositing Cu and Fe particles under mechanochemical conditions followed

by a calcination at 400 °C. Slightly lower ML yields (58 %) were observed for Cu/HZSM and

slightly higher for Fe/HZSM-5-50 (63 %). This difference was rather small and therefore

commercial H-ZSM-5-50 was used for the experiments in continuous flow mode.

Continuous flow alcoholysis. First, the effect of the hydrodynamic pressure was studied

during 2-3 h continuous flow alcoholysis using a 0.2 M FA feedstock in MeOH. The results

(**Figure 2**) show that *ca.* 12 % more ML was produced, *ca.* 5% less AL and *ca.* 8 % less reaction

intermediates when the pressurization was set at 50 bars. The selectivity to AL was substantial

lower in continuous flow mode compared to the batch experiments, in favor of the ML yield

which was 11-15 % higher (at 50 bars) than in batch. To further optimize the reaction conditions,

feedstocks with increasing loads of FA (0.1-1.6 M) were tested at different flow rates (0.2-0.5 mL min^{-1}). The results show that conversions stayed close to 100 % at FA concentrations from 0.1 to 0.8 M whereas with 1.6 M feedstocks the conversion started to drop with higher flow rate (**Figure 3a**). Surprisingly, at least at low flow rate (0.2 mL min^{-1}), the yield to the target product ML increased when using higher FA loads (**Figure 3b**). This effect tended to be less pronounced when moving to high flow rate (0.5 mL min^{-1}). Another effect of increasing the flow rate was that the AL yields slightly increased, except at 1.6 M FA load (**Figure 3c**). The reaction intermediate MMF (**Figure 3d**) was only detected when using FA loads of 0.8 M. At 1.6 M FA load the MMF yield dropped again. These results indeed suggest that α-angelica lactone is no reaction intermediate but a side product arising from levulinic acid. The reason why its yield increases with higher flow rate remains not fully clear, but it may be related to water residues present in the alcohol feedstocks. The results also demonstrate that, when working with methanol in continuous flow, feedstocks with high FA load (1.6 M) can be converted efficiently, at least when working at low flow rate (0.2 mL min^{-1}). The relations between the product yield and the weight hourly space velocity (WHSV) at increasing FA loads and increasing flow rate are illustrated in **Figure 4a** and **Figure 4b**, respectively. WHSV (g g^{-1} h^{-1}) is the mass feed rate of FA (g h^{-1}) divided by the amount of catalysts (g) to which FA is fed; it allows to compare the catalytic activity in continuous flow. The results show that the alcoholysis rate increases with the FA concentration until a certain breaking point between 0.8 and 1.6 M. Feed solutions of 0.8 and 1.6 M FA correspond with MeOH:FA molar ratios of 29 and 13, respectively. In comparison, previously reported batch results employed alcohol excess of 24 (MeOH:FA).[14] Finally, the effect of the reaction temperature was studied (**Figure 5**) using a high load feed solution (1.6 M). The results show that temperatures *ca.* 150 °C are required to fully convert the FA into ML (only

small amount of reaction intermediates left). The yield of ML increased further at 170 °C, but significant amounts of polyfurfuryl alcohols started to form at this temperature. At 90 °C the yield of β-angelica lactone (BAL) was low but then started to increase with increasing temperature, because the isomerization of α-angelica lactone (AAL) to BAL was favored at higher temperature, in agreement with the literature.[32] At temperatures ≥ 150 °C the BAL yields dropped again.

((Figure 2))

((Figure 3))

((Figure 4))

((Figure 5))

The operational stability of a catalytic bed packed with H-ZSM-5-50 was subsequently studied during 2-3 h on stream under optimized conditions (1.6 M, 170 °C, 0.2 mL min^{-1}, 50 bars, **Figure 6a**). Unfortunately, after 1 h the conversion and products yields started to drop pronouncedly and instead the MMF reaction intermediate started to build up but then also further

decreased until the catalytic bed was fully deactivated. When using a 0.2 M FA feedstock instead (**Figure 6b**), the conversion remained stable over 9 hours at least, with mean yields 71 and 23 % for ML and BAL, respectively. The thermogravimetric analysis of the catalysts used with different FA loads (**Figure 7a**), shows the build-up of polyfurfuryl alcohols when using feed solutions with higher FA loads. Their color turned from white (zeolite) to purple (1.6 M). Based on the FA mass intake after 1.3 h continuous flow, one can see that only with 1.6 M FA significant amounts (0.5 wt% on FA intake) of polymeric material was formed (**Figure 7b**), enough to deactivate the catalyst. With 0.4 M FA the amount of polyfurfuryl alcohol formed was only 0.15 wt%. After recalcination at 800 °C for 8 h of the catalyst used in the experiment with 1.6 M FA and re-utilization with a 0.2 M FA feedstock, the initial catalytic activity (**Figure 8a**) was recovered, although not fully (**Figure 8b**). A better catalyst regeneration was achieved by recalcination at lower temperature (500 °C) and during shorter time (4 h), as the product distribution (**Figure 8c**) was almost identically as compared to the experiment before the catalyst regeneration. A comparison of the XRD spectra (**Figure S2**) of pristine, used and regenerated H-ZSM-5-50 showed that their crystallinity was retained at any time, which demonstrates the robustness of this zeolite and which suggests that the formation of polyfurfuryl alcohol was the only cause of catalyst deactivation.

((Figure 6))

((Figure 7))

((Figure 8))

Finally, the continuous flow alcoholysis using H-ZSM-5-50 was also tested in ethanol and *n*-propanol to study the effect on the catalytic activity (**Table 2**). The alkyl levulinates yield dropped 19-20 %, while the angelica lactones yield remained the same in ethanol (21-23 %) while it dropped to 8 % in *n*-propanol. In both experiments, more than 95 % of the angelica lactones consisted of BAL. Instead, some other weak signals appeared of unidentified peaks appeared in the chromatograms of the alcoholysis product in ethanol and *n*-propanol.

CONCLUSIONS

Two FAU zeolites and two MFI zeolites were tested for the catalytic alcoholysis of 0.2 M furfuryl alcohol in methanol, yielding methyl levulinate (ML), α-angelica lactone (AAL) as the side product from levulinic acid dehydration and β-angelica lactone (BAL) as the corresponding isomerization product, along with some reaction intermediates. H-ZSM-5-50 zeolite (SiO_2/Al_2O_3 molar ratio 50) showed the best activity with 60 % ML and 33 % BAL yields after 5 min microwave irradiation at 150 °C. A modified zeolite catalyst (Fe/H-ZSM-5-50), resulted in higher ML yield (63 %) and lower BAL yield (28 %). Using a catalytic bed packed with H-ZSM-5-50 catalyst in continuous flow, higher selectivity to ML and lower selectivity to angelica lactones was observed, at least for flow rates up to 0.4 mL min^{-1}. Interestingly, at 0.2 mL min^{-1}, high feed loads up to 1.6 M FA were converted efficiently (79 % ML yield), but faced the build-

up of polyfurfuryl alcohol. The initial activity of the used ZSM-5-50 catalyst was restored by regeneration at 500 °C. Finally, the alcoholysis in ethanol and *n*-propanol under identical conditions yielded 20 % less alkyl levulinate and similar yield of angelica lactones in ethanol, but 13 % less in *n*-propanol.

ASSOCIATED CONTENT

Supporting Information

ACKNOWLEDGEMENTS

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Table 1. Acid catalysts reported for the conversion of furfuryl alcohol (FA) to alkyl levulinates (AL).

Entry	Catalyst (load, %)[a]	Conditions	FA (M)	ROH:FA molar ratio	AL yield (%)[b]	Ref.
1	H_2SO_4 (8)	130 °C, 2 h	0.4	24 (MeOH)	50	[14]
2	SO_4-ZrO_2 (8)	130 °C, 2 h	0.4	24 (MeOH)	73	[14]
3	[BMIm-SH][HSO_4] (8)	130 °C, 2 h	0.4	24 (MeOH)	94	[14]
4	Al-TUD-1 (34)	140 °C, 2 h	0.3	57 (EtOH)	48	[15]
5	$H_3PW_{12}O_{40}$ (1.5)	120 °C, 2 h	0.2	60 (EtOH)	63	[16]
6	$AlCl_3$ (10)	110 °C, 2 h	0.3	55 (EtOH)	69	[17]
7	α-Fe_2O_3 (3500)	250 °C, 1 h	0.02	745 (EtOH)	73	[18]
8	Graphene oxide (25)	120 °C, 2 h	0.3	51(EtOH)	78	[19]
9	HCl (39)	120 °C, 2 h	0.2	60 (EtOH)	87	[16]
10	Amberlyst^{TM}-15 (1.5)	120 °C, 2 h	0.2	60 (EtOH)	88	[16]
11	[(HSO_3-p)$_2$im][HSO_4] (12)	110 °C, 2 h	0.4	44 (EtOH)	92	[20]
12	γ-Fe_2O_3/H-ZSM-5 (39)	130 °C, 2 h	0.2	55 (2-BuOH)	63	[21]
13	Amberlyst^{TM}-70 (25)	110 °C, 2 h	0.3	33 (1-BuOH)	68	[4]
14	$CuCl_2$ (9)	115 °C, 2 h	0.3	35 (1-BuOH)	81	[22]
15	SBA-15-SO_3H (25)	110 °C, 2 h	0.3	33 (1-BuOH)	83	[4]

[a] Weight percentage on FA load; [b] molar percentage

Table 2. Effect of alcohol chain length in continuous flow alcoholysis at 170 °C and 50 bars using 1.6 M FA at 0.2 mL min^{-1} feed rate and 200 mg H-ZSM-5-50.

Entry	Alcohol	Conversion (%)	Yield (%)		
			Levulinate[a]	Angelica lactones	Alkoxymethylfuran[b]
1	Methanol (C1)	100	79	21	0
1	Ethanol (C2)	100	59	23	1
2	n-Propanol (C3)	100	60	8	2

[a] methyl/ethyl/n-propyl levulinate; [b] 2-methoxy/ethoxy/n-propoxy-2-methylfuran

Scheme 1. Production of biomass derived alkyl levulinates via (a) esterification of levulinic acid, (b) alcoholysis of 5-hydroxymethylfurfuryl alcohol (in green) and (c) alcoholysis of furfuryl alcohol (in blue).

Figure 1. Methyl levulinate (ML), α-angelica lactone (AAL), β-angelica lactone (BAL) and 2-methoxy-2-methylfuran (MMF) yields obtained after 5 min batch alcoholysis of 0.2 M furfuryl alcohol (FA) assisted by microwave irradiation in methanol (MeOH) at 150 °C using 50 mg of zeolite catalyst.

Figure 2. Effect of hydrodynamic pressurization on ML and BAL yields over 2 h on stream in continuous flow alcoholysis at 170 °C using 200 mg H-ZSM-5-50 and 0.2 M FA in MeOH at 0.2 mL min^{-1} feed rate.

Figure 3. Effect of FA load in MeOH and flow rate on (a) conversion and yields of (b) ML, (c) BAL and (d) MMF, observed in continuous flow alcoholysis at 170 °C and 50 bars using 200 mg H-ZSM-5-50.

Figure 4. Evolution the ML yield with the weight hourly space velocity (WHSV, g g^{-1} h^{-1}) at different flow rates, as observed in continuous flow alcoholysis at 170 °C and 50 bars using 200 mg H-ZSM-5-50.

Figure 5. Effect of reaction temperature on conversion and product yields in continuous flow alcoholysis using 200 mg H-ZSM-5-50 and 1.6 M FA in MeOH at 0.2 mL min^{-1} feed rate.

Figure 6. Operational stability in continuous flow alcoholysis experiments at 170 °C and 50 bars using 200 mg H-ZSM-5-50 and (a) 1.6 M FA and (b) 0.2 M FA, both in MeOH at 0.2 mL min^{-1} feed rate.

Figure 7. Weight loss observed during thermogravimetric (TGA) analysis from fresh and used H-ZSM-5-50 catalyst recovered after continuous flow alcoholysis (170 °C, 50 bars, 0.2 mL min^{-1}), using different feed loads of FA in MeOH.

Figure 8. Comparison of catalytic activity in continuous flow alcoholysis of 0.2 M FA in MeOH (170 °C, 50 bars, 0.2 mL min^{-1}), using 200 mg of (a) H-ZSM-5-50, H-ZSM-5-50 recovered after 1.3 h on stream in continuous flow alcoholysis (170 °C, 50 bars, 0.2-0.5 mL min^{-1}) using a 1.6 M FA feedstock, followed by calcination at (b) 800 °C for 9 h and (c) 500 °C for 4 h.