



Feature Article

One-step Pd/C and Eu(OTf)₃ catalyzed hydrodeoxygenation of branched C₁₁ and C₁₂ biomass-based furans to the corresponding alkanes



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ABSTRACT

Solvent-free NaOH catalyzed aldol condensation of biomass-derived 5-hydroxymethyl furfural (HMF) and furfural with methyl isobutyl ketone (MIBK) was studied, producing branched C₁₁ and C₁₂ furan compounds in high yields of up to 96%. Through use of a Pd/C and Eu(OTf)₃ catalytic system, the condensation products of the bio-based starting materials were further hydrodeoxygenated (HDO) in one-step to biofuel compatible branched alkanes 2-methylundecane (**3**) and 2-methyldecane (**4**) in excellent yields of 90% and 98%, respectively. In the one-step HDO developed herein, the variation of solvent had a significant effect on the reaction route and degree of conversion of furans to alkanes in the HDO process. Very high overall yields of alkanes **3** (86%) and **4** (94%) were obtained starting from the biomass-based HMF and furfural.

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1. Introduction

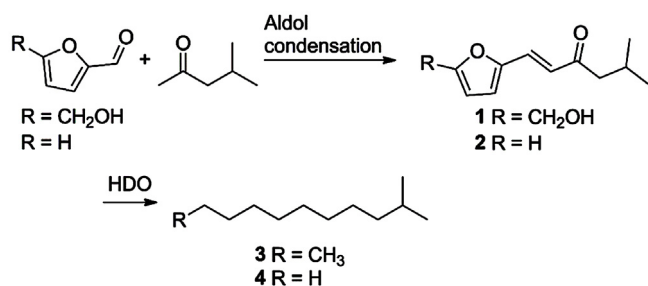
The aspiration for sustainable development directs the research towards the development of new sustainable, carbon neutral feedstocks that can be used as substitutes for crude oil. Lignocellulosic biomass, consisting mostly of cellulose, hemicellulose and lignin, is cheap, non-edible and abundant which makes it ideal source for renewable chemicals [1,2]. Isolated polysaccharide chains, cellulose and hemicellulose, can be hydrolyzed to their structural monosaccharides, mainly glucose and xylose, which can be catalytically dehydrated into HMF and furfural respectively [3]. HMF and furfural are considered as important biomass-derived platform chemicals in vast array of value-added chemical, polymer and biofuel applications [4,5]. The dehydration of glucose and fructose to HMF has been under intense examination lately and good yields have been obtained on a laboratory scale [3,6–8]. However, large scale production remains a challenge due to inefficient HMF purification methods and low process yields [9]. In contrast, furfural is produced on an industrial scale using lignocellulosic material from various sources [5].

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Hydrodeoxygenation (HDO) is an attractive method to further convert biomass-derived multifunctional raw materials to corresponding alkanes [10–12]. In HDO processes heterocycles are opened, double bonds are saturated, and oxygen containing functionalities are simultaneously removed. Various HDO systems have been reported using nickel and palladium as well as other noble metal based hydrogenation catalysts [13–20]. The impacts of broad set of cocatalysts, including metal triflates, acidic support materials and Brønsted acids have also been studied [15–19,21]. Brønsted acids are mainly used to open 2,5-disubstituted furans, while use of metal triflates can effectively catalyze the ring opening and deoxygenation of the less reactive species such as tetrahydrofuran rings (THF) [15–19,21,22]. The use of metal triflates as cocatalysts results in high product selectivity and yield as the skeletal transformation through isomerization is reduced [15,19]. In general, the high temperatures and long reaction times required for HDO can reduce the selectivity and the efficiency of the conversion of furans to alkanes. The main focus of the furan-based HDO research has been on the use of HMF-derived compounds as substrates, while industrially available furfural and its derivatives have drawn less attention.

Herein, we present a highly efficient approach for the synthesis of branched C₁₁ and C₁₂ biofuel compatible alkanes from biomass-based chemicals. The procedure consists of optimized aldol condensation of HMF and furfural with MIBK in mild solvent-free reaction conditions, followed by new high yield one-step HDO,



Scheme 1. The high yield two-step procedure from biomass-based furans to branched C₁₁ and C₁₂ alkanes.

producing alkanes in high overall yields of 86% and 94% from HMF and industrially available furfural respectively (Scheme 1).

2. Methods and materials

2.1. General procedure for the synthesis of **1** and **2**

Desired amount of HMF/furfural (furfural ($\geq 98\%$), HMF (99%) Sigma Aldrich), MIBK ($\geq 98.5\%$ Sigma Aldrich) and base catalyst (NaOH ($\geq 98\%$), KOH (90%) and K₂CO₃ (99%) Sigma Aldrich, Na₂CO₃ ($\geq 99.5\%$) Fischer and Ca(OH)₂ (96%) Merck) were placed in this order into an 8 ml glass vial with a magnetic stirring bar and the vial was closed with a cap. The mixture was heated at appropriate temperature in an oil bath with a thermostat and the stirring was set to 900 rpm (See SI for more details). After the required time, the reaction solution was cooled down to room temperature and EtOAc (5 ml) was added, followed by washing with saturated aqueous NaCl-solution (2 ml). The washing solution was extracted with ethyl acetate (EtOAc, 3 \times 5 ml). The organic layers were combined and the solvents were evaporated *in vacuo* to give the desired products **1** and **2** as dark-brownish oils. To determine the yields, the products were dissolved in EtOAc (5 ml). From this solution, an aliquot of 0.5 ml was taken, 0.1 ml of internal standard (acetophenone) was added and the resulting solution was diluted with EtOAc (10 ml). The yields of **1** and **2** were determined from this solution with GC-FID.

2.2. General Procedure for HDO of **1** and **2** to **3** and **4**

Desired amount of substrate (**1** or **2**) was weighed and placed into the furnace insert with magnetic stirring bar. After this, appropriate amount of solvent, cocatalyst (HOTf ($\geq 99\%$), Eu(OTf)₃ (98%), YbCl₃ (99.9%), Nd(OTf)₃ (98%), FeCl₃ (97%) Sigma Aldrich; Hf(OTf)₄ (98%), Fe(OTf)₃ (90% tech.), EuCl₃ (99.9%), Sc(OTf)₃ (98%), Y(OTf)₃, LaCl₃ (99.9%) and La(OTf)₃ (99%) Alfa Aesar; InCl₃ (98%) Fluka; and AlCl₃ (98.7%) Baker) and 0.4 mol-% of Pd/C (5 w-%, Sigma Aldrich) were added. The glass insert was placed into the autoclave, which was then closed and placed into a heating mantle (Roth 30S). The autoclave was pressurized with H₂ to 40 bars (at room temperature) and heated at 200 °C for desired time (See SI for more details). After heating, the reaction solution was cooled to room temperature, filtered and diluted with EtOAc or hexane (depending on the solvent used) to 50 ml. From this solution, an aliquot of 1.25 ml was taken, 0.1 ml of internal standard (acetophenone) was added and the resulting solution was diluted with EtOAc or hexane (10 ml). The yields of **3** and **4** were determined from this solution with GC-FID.

2.3. Analysis

The yields of aldol condensation products **1** and **2** as well as alkanes **3** and **4** were determined by a gas chromatograph equipped

with a flame ionization detector (GC-FID). The GC-FID runs were performed using Agilent Technologies 6890N Network GC System fitted with Agilent HP-INNOWAX column (length 30 m, internal diameter 0.25 mm and stationary phase thickness 0.25 μm). The calibration curves were plotted using standard samples with different concentrations of HMF (99%, Sigma Aldrich), furfural ($\geq 98\%$, Sigma Aldrich), pure **1** (column chromatography, EtOAc: hexane 1:1.5, R_f = 0.33), **2** (distillation *in vacuo*, bp. 96–97 °C at 1.5 mbar) and pure 2-methyldecane (**4**) to calculate the selectivities, conversions and yields (See SI for more details). The yield of **3** was determined from the calibration curve prepared from pure **4**.

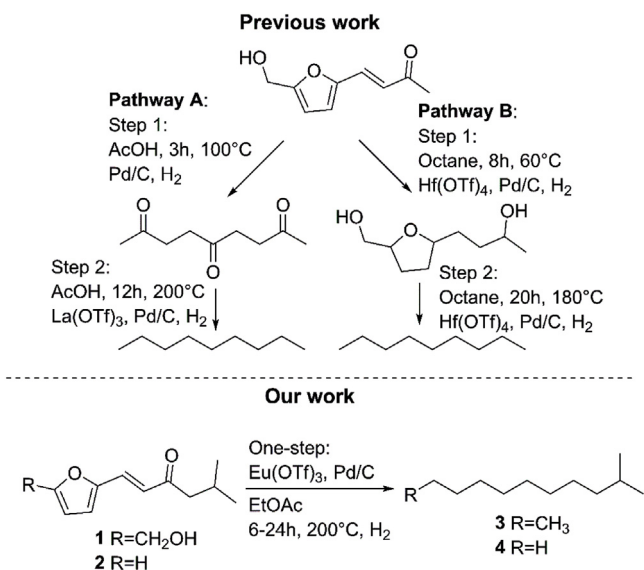
3. Results and discussion

The aldol condensation of biomass-derived furfurals and ketones is a classical, efficient and straightforward method of combining aldehydes and ketones. In respect to biofuel research, alkaline aqueous biphasic aldol condensations of furfurals and acetone as well as other ketones have been examined [23,24]. In particular, the focus has been on the aldol condensation of acetone with furfurals using different heterogeneous Brønsted catalysts such as Mg-Al-oxide, MgO-ZrO₂ and Nit-NaY (nitrogen-substituted zeolite) [13,25,26]. As in fuel applications branched alkanes are preferred over linear alkanes due to their lower melting points and higher octane numbers. In this respect, MIBK is an attractive choice of substrate for the production of branched C₁₂ and C₁₁ furans via the aldol condensation of HMF and furfural. In addition, MIBK is available from acetone (product of acetone-butanol-ethanol fermentation), it is regarded as a biomass-based chemical [27,28].

We initiated the study by investigating a solvent-free aldol condensation of HMF and furfural with MIBK using NaOH as a Brønsted catalyst. Under the optimized reaction conditions (50 °C, 6 h, molar ratio of 1:4 (furfurals:MIBK) and 13 mol-% of NaOH, See Scheme 1, page S7 and Table S2 in SI), the products **1** and **2** were obtained in excellent yields of 95% and 96% respectively. Due to the absence of water, the amount of NaOH catalyst was significantly reduced in comparison to earlier reports on biphasic aldol condensations of HMF (97 mol-% of NaOH) and furfural (37 mol-% of NaOH) [23,24]. Based on product analysis (GC-FID, ¹H NMR) we did not observe any condensation of the secondary α -carbon. However, minor quantities of Cannizzaro reaction products (~ 2 mol-%) were extracted from the acidified water phase (¹H & ¹³C NMR) [29,30].

In the reports of Sutton et al. and Song et al. the HDO reactions were conducted in two steps, in which the reaction routes depended on the used solvent (Scheme 2) [15,19]. The use of acetic acid (AcOH) as a solvent promotes Brønsted acid catalyzed ring-opening of the 2,5-disubstituted furans, such as **1**, to acyclic polyketones, which are then hydrogenated to polyols with H₂-Pd/C, followed by acetoxylation of the hydroxyl groups with AcOH (Scheme 2, Pathway A) [15,31,32]. In the second step at higher temperatures the La(OTf)₃ cleaves the acetates and the desired alkane is obtained through reduction of the formed C–C double bonds [15,32]. In contrast, in aprotic solvents such as *n*-octane, the similar HMF-based substrate is first hydrogenated to the corresponding THF compound (Scheme 2, Pathway B) [19]. In the second step at higher temperatures, alkanes are formed through the Hf(OTf)₄ catalyzed cleavage of the cyclic ether and the alcohol C–O bonds, followed by hydrogenation of the C–C double bonds formed by H₂-Pd/C (Scheme 2) [19,21].

We investigated the one-step HDO of **1** and **2** using Pd/C and metal triflates as catalysts. First, we studied Pathway A conditions (Scheme 2) for the two-step HDO of both HMF-based **1** and furfural-based **2** using AcOH as a solvent and La(OTf)₃ as a cocatalyst [15]. Under these conditions alkanes **3** and **4** were obtained in fair yields of 49% and 51% respectively. Interestingly, ¹H NMR studies after



Scheme 2. The reaction pathways for metal triflate catalyzed two-step HDO of furans to alkanes (Pathway A and B) and the one-step HDO developed in this study.

the first step (100 °C, 4 bar H₂) revealed that the 2,5-disubstituted **1** formed a mixture of cyclic and acyclic products through partial Brønsted acid catalyzed furan ring-opening, whereas the mono-substituted **2** was solely hydrogenated to the corresponding THF derivative (See Figs. S21 and S22 in SI). The different reactivity of **1** and **2** in AcOH apparently depended on the substituent patterns of the furan. These observations were in agreement with previous studies on the Brønsted acid catalyzed ring-opening of furans [15,17]. It should be noted that, after the second step (200 °C, 20 bar H₂, 12 h) ¹H NMR and ¹³C NMR analysis of the crude product showed the presence of acetylated intermediates. This indicates that the HDO reaction was not complete, thus explaining the moderate yields of **3** and **4** (See Figs. S27–S30 in SI).

Based on the preliminary results above, there was no apparent reason for separating HDO into two different steps, but rather to simplify the procedure into one step. Therefore we investigated the impact of various cocatalysts on the one-step HDO outcome at 200 °C using **2** as the substrate and AcOH as the solvent (Table 1).

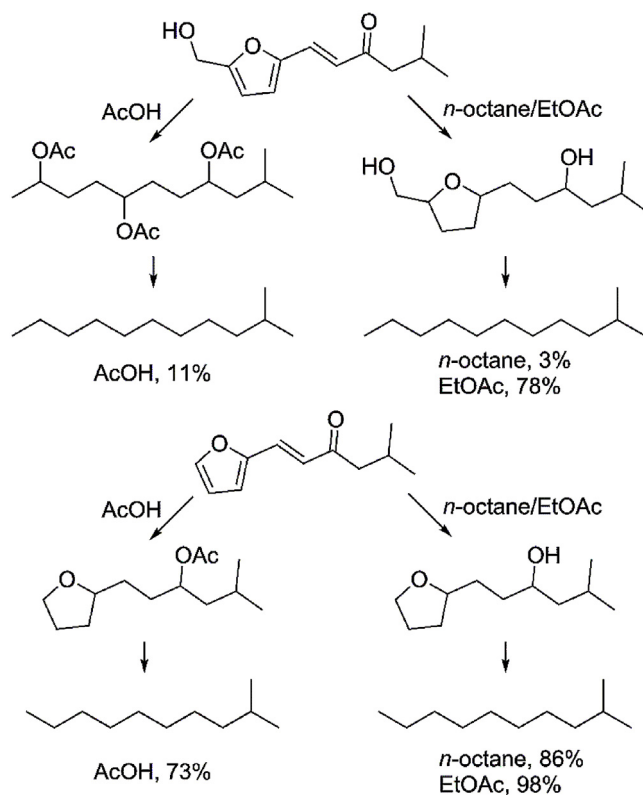
Table 1
The results of cocatalyst screening in AcOH.^a

Entry	Substrate	Cocatalyst	Alkane yield (%) ^b
1	2	La(OTf) ₃	53
2	2	Eu(OTf) ₃	73
3	2	Fe(OTf) ₃	35
4	2	Y(OTf) ₃	21
5	2	Sc(OTf) ₃	49
6	2	Nd(OTf) ₃	59
7	2	Hf(OTf) ₄	18
8	2	EuCl ₃	2
9	2	FeCl ₃	7
10	2	LaCl ₃	9
11	2	–	0
12	2	HOTf	49

Full conversion of the substrate was detected in all of the experiments.

^a Reaction conditions; **2** as substrate: 5.7 mmol of **2**, 0.4 mol-% of Pd/C (5 w-%), 16 h at 200 °C, 15 mol-% of M(OTf)_x, 40 bar H₂ (at rt.), 15 ml of AcOH.

^b Yields obtained with GC-FID using calibration curves.



Scheme 3. Overview of the effect of solvents and substituents on the one-step HDO of **1** and **2** to **3** and **4**.

Given the promising results generated with La(OTf)₃, we focused on various metal triflates.

In the selected reaction conditions (AcOH, 200 °C, 40 bar H₂, 0.4 mol-% Pd/C) Eu(OTf)₃ was the most active cocatalyst in one-step HDO, affording **4** in 73% yield (Table 1, Entries 1–7). Notably, Eu(OTf)₃ was clearly more efficient than the previously reported La(OTf)₃ and Hf(OTf)₄ [15,19]. The unexpected low yield of 18% obtained using Hf(OTf)₄ is due to the hampering effect of AcOH as a polar solvent coordinating to the hafnium metal center [21,33]. In comparison to triflates, very low yields of **4** were obtained with the corresponding metal chlorides (Entries 8–10). It is noteworthy that no alkane was formed in the absence of the cocatalyst, and the use of triflic acid (HOTf) led to only fair yield of **4** (Entries 11–12). These results highlight the importance of the triflate anion in combination with Lewis acid metal cation. Increased catalytic activity of the metal triflates is attributed to the strong electron-withdrawing capacity of the triflate anion which imparts Lewis acid character to the metal center resulting in more efficient coordination to the free electron pairs of the oxygen atom [34]. In the series of lanthanides, Eu³⁺ has high Lewis acidity and low oxophilicity, which could explain the tolerance towards coordinating solvents [35].

To increase the product yield, we next studied the effect of different solvents, including AcOH, *n*-octane and EtOAc, and their mixtures using Eu(OTf)₃ as cocatalyst (Table 2, See Table S3 in SI).

We found that the solvent had a crucial effect on the reaction outcome with both **1** and **2** as substrates. The change of solvent from AcOH to *n*-octane improved the yield of **4** from 73% to 86%, as the deoxygenation pathway was altered from acetoxylation-deacetylation sequence in AcOH to metal triflate catalyzed alcohol C–O cleavage in *n*-octane (Scheme 3, Table 2, Entries 1–3) [19,21,32]. Surprisingly, the yield of **4** was further increased to 98% using EtOAc, in which, hypothetically, the HDO proceeds in a similar route to that in *n*-octane (Entry 4). In the case of **1**, the change of AcOH to *n*-octane decreased the yield of **3** from 11% to

Table 2
Summarized results of the effect of solvents on **3** and **4** yields with $\text{Eu}(\text{OTf})_3$.^a

Entry	Substrate	Solvent	Solvent Ratio (V:V)	Alkane yield (%) ^b
1	2	AcOH	–	73
2	2	AcOH – <i>n</i> -octane	1:1	80
3	2	<i>n</i> -octane	–	86
4	2	EtOAc	–	98 (94)
5	1	AcOH	–	11
6	1	AcOH – <i>n</i> -octane	1:1	40
7	1	<i>n</i> -octane	–	3
8	1	EtOAc – <i>n</i> -octane	1:1	65
9	1	EtOAc	–	78
10 ^c	2	Solvent-free	–	53

Full conversion of the substrate was detected in all of the experiments.

^a Reaction conditions; **1** as substrate: 3.4 mmol of **1**, 0.4 mol-% of Pd/C (5 w-%), 16 h, 200 °C, 40 bar H_2 (at rt.), 15 mol-% $\text{Eu}(\text{OTf})_3$, 10 ml solvent volume, **3** as product; **2** as substrate: 5.7 mmol of **2**, 0.4 mol-% Pd/C (5 w-%), 16 h, 200 °C, 40 bar H_2 (at rt.), 15 mol-% $\text{Eu}(\text{OTf})_3$, 15 ml solvent volume, **4** as product.

^b Yields obtained with GC-FID using calibration curves, isolated yields in brackets (See page S16 in SI).

^c 17.2 mmol of **2**, 0.1 mol-% of Pd/C (5 w-%), 0.6 mol-% of $\text{Eu}(\text{OTf})_3$, 200 °C, 28 h, 40 bar H_2 (at rt.).

3% due to the low solubility of the substrate (Entries 5 & 7). The addition of AcOH or EtOAc to *n*-octane (1:1, v:v) increased the solubility of **1** and improved the yields of **3** to 40% and 65% respectively (Entries 6 & 8). As with **4**, the highest 78% yield of **3** was obtained in EtOAc (Entry 9). We assumed that the higher yields of **3** and **4** obtained in non-acidic solvents (EtOAc and the mixtures of *n*-octane and EtOAc vs. AcOH) was due to diminished Brønsted acid catalyzed furan ring-opening combined with more facile cleavage of alcohols than acetates.

To establish the HDO reaction routes for **1** and **2** in EtOAc, we conducted mild temperature reactions to identify possible intermediate species (100 °C, 4 h, 40 bar H_2 , 15 mol-% $\text{Eu}(\text{OTf})_3$, 0.4 mol-% Pd/C). Based on ^{13}C NMR analysis, both **1** and **2** were hydrogenated to the corresponding THF derivatives (See Figs. S32 and S33 in SI), thus supporting our assumption. Subsequently, at high temperature HDO, the $\text{Eu}(\text{OTf})_3$ is likely to catalyze the ring-opening of THF and the removal of the hydroxyl groups in a similar manner to that proposed for $\text{Hf}(\text{OTf})_4$ (Scheme 4) [19,21]. In this respect it is worth noting, that at mild temperatures THF compounds can also undergo direct hydrogenolysis into open chain alcohols when catalyzed by the combination of noble metals and low-valent metal oxides as reported by Tomishige group [36–38]. Overall, higher alkane yields were obtained in solvents, where the HDO of both **1** and **2** proceeds through THF intermediates followed by the metal catalyzed cleavage of the alcohol C–O bonds (Scheme 3, EtOAc and *n*-octane vs. AcOH). The improved yields of **3** and **4** obtained in EtOAc over *n*-octane can be ascribed to the polar nature of the solvent. EtOAc has higher polarity than *n*-octane and thus offers increased solvation of the substrates as well as greater stabilization of the carbocation transition states present during HDO [39]. Unfortunately, in the presence of $\text{Eu}(\text{OTf})_3$ simultaneous formation of ethanol and AcOH (8 mol-% according to GC-MS/FID studies) was observed, presumably arising from metal triflate catalyzed ester cleavage of EtOAc [32,33,40].

The effect of the reaction time, the amount of $\text{Eu}(\text{OTf})_3$ and the H_2 pressure on the one-step HDO reaction outcome were investigated (200 °C, 40 bar H_2 , 0.4 mol-% Pd/C in EtOAc or *n*-octane).

With the monosubstituted furan **2** as a substrate, the reaction time could be reduced from 16 h to 6 h in both EtOAc and *n*-octane with no decrease in the yields of **4** (Table 3, Entries 1–6). This is a significantly shorter time than generally required for the HDO of furan compounds. With shorter than 6 h reaction times in EtOAc, the yield of **4** builds up steadily from 29% up to 93% during 1–4 h. In all of the time on stream experiments full conversion of **2** through

Pd/C catalyzed hydrogenation was detected (Fig. 1). These results show that the Pd/C catalyzed hydrogenation is fast compared to the $\text{Eu}(\text{OTf})_3$ catalyzed C–O bond cleavages, which seems to limit the formation of **4**. The use of 5 mol-% of $\text{Eu}(\text{OTf})_3$ instead of 15 mol-% decreased the yield of **4** substantially from 98% to 53% (Entries 1 & 8). Also, when the H_2 pressure was lowered from 40 bars to 20 bars, the yield of **4** was reduced from 97% to 73% (Entry 3 & 10). With regards to the 2,5-disubstituted furan **1**, the 6 h reaction time was too short and only a 36% yield of **3** was detected. By extending the reaction time to 16 h and 24 h the yield was improved significantly to 78% and 90% respectively (Entries 11–13). The longer reaction time required with **1** can be explained by the presence of the primary hydroxyl group, which is more resistant to cleavage than the secondary one (See Fig. S31 in SI) [21,41]. The conversion of furfural-based **2** to acyclic alkane is more facile than that of HMF-based **1**. Overall, under the optimized one-step HDO reaction conditions the developed catalytic system converted the unsaturated furan compounds efficiently into the corresponding alkanes with similar, very high, yields as previously reported for two-step systems [15,19].

The recyclability of the Pd/C and $\text{Eu}(\text{OTf})_3$ catalysts was investigated by conducting four consecutive runs under the optimal conditions using **2** as a substrate (Fig. 2, Table 3, See page S16 and

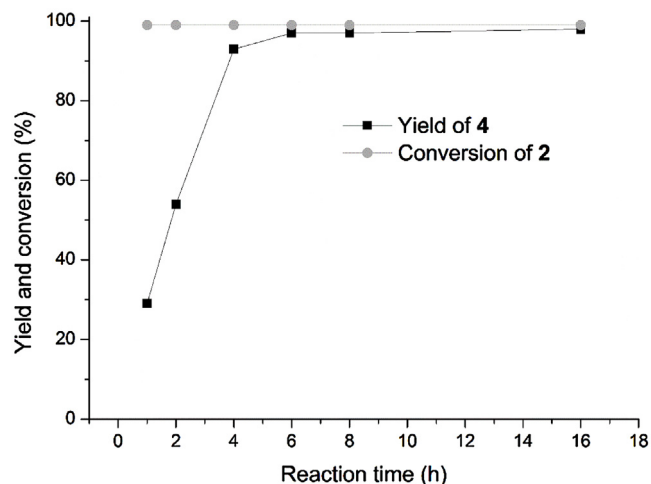
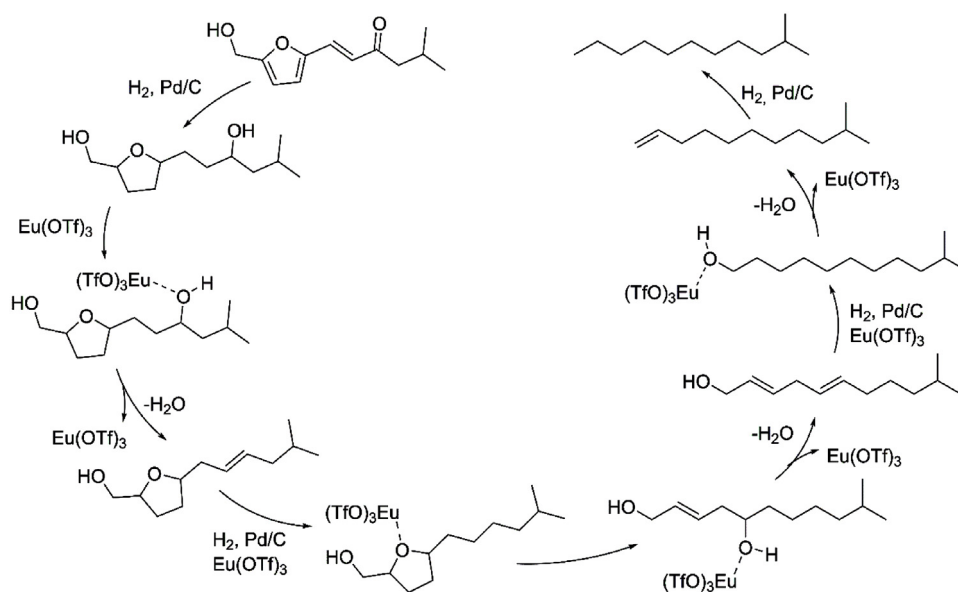


Fig. 1. Catalytic performance as a function of time on stream using **2** as a substrate and EtOAc as a solvent.



Scheme 4. Putative reaction pathway of the one-step HDO in EtOAc using **1** as substrate.

Table 3

The effect of reaction time, the amount of $\text{Eu}(\text{OTf})_3$ and H_2 pressure on the alkane yield in the one-step HDO.^a

Entry	Substrate	Solvent	$\text{Eu}(\text{OTf})_3$ (mol-%)	Time (h)	Alkane yield (%) ^b
1	2	EtOAc	15	16	98 (94)
2	2	EtOAc	15	8	97
3	2	EtOAc	15	6	97
4	2	EtOAc	15	4	93
5	2	<i>n</i> -octane	15	16	86
6	2	<i>n</i> -octane	15	6	85
7	2	<i>n</i> -octane	5	6	58
8	2	EtOAc	5	16	53
9 ^c	2	EtOAc	5	6	66
10 ^d	2	EtOAc	15	6	73
11	1	EtOAc	15	6	36
12	1	EtOAc	15	16	78
13	1	EtOAc	15	24	90 (86)
14	2	2nd run <i>n</i> -octane	15	6	80
15	2	3rd run <i>n</i> -octane	15	6	20

Full conversion of the substrate was detected in all of the experiments.

^a Reaction conditions; **1** as substrate: 3.4 mmol of **1**, 0.4 mol-% of Pd/C (5 w-%), 200 °C, 40 bar H_2 (at rt.), 15 mol-% $\text{Eu}(\text{OTf})_3$, 10 ml EtOAc, **3** as product; **2** as substrate: 5.7 mmol of **2**, 0.4 mol-% Pd/C (5 w-%), 200 °C, 40 bar H_2 (at rt.), 15 mol-% $\text{Eu}(\text{OTf})_3$, 15 ml EtOAc/*n*-octane, **4** as product.

^b Yields obtained with GC-FID using calibration curves, isolated yields in brackets (See page S16 in SI).

^c EtOAc volume 5 ml.

^d 20 bar H_2 (at rt.).

Table S3 in SI). After the first run, the catalysts remained active and only a slight decrease of 5% was observed in the yield of **4** in the second run (Entries 6&15). However, drastic inactivation of the catalyst system was observed after the third run and only a 20% yield of **4** was obtained (Entry 15). In all of the recycling experiments full conversion of **2** into hydrogenated intermediates was detected, indicating that $\text{Eu}(\text{OTf})_3$ is deactivated rather than Pd/C (Fig. 2). The formed side products can cause the poisoning of the $\text{Eu}(\text{OTf})_3$, for example, through anion exchange. The catalytic activity could not be restored by washing and heating the catalyst *in vacuo*, thus the regeneration of the catalyst system remains a challenge.

4. Conclusions

As shown herein NaOH catalyzed solvent-free aldol condensation enables efficient conversion of biomass-based substrates into branched C_{11} and C_{12} furan compounds, **1** and **2**, in high yields of 95% and 96% respectively. We developed high yield one-step HDO of the condensation products involving Pd/C and $\text{Eu}(\text{OTf})_3$ catalysts in the green solvent EtOAc. Under optimized conditions excellent yields of alkanes **3** (90%) and **4** (98%) were obtained. The combined yields of the solvent-free aldol condensation and the one-step HDO corresponds to the very high overall yields of **3** (86%) and **4** (94%) starting from the respective biomass-based furans.

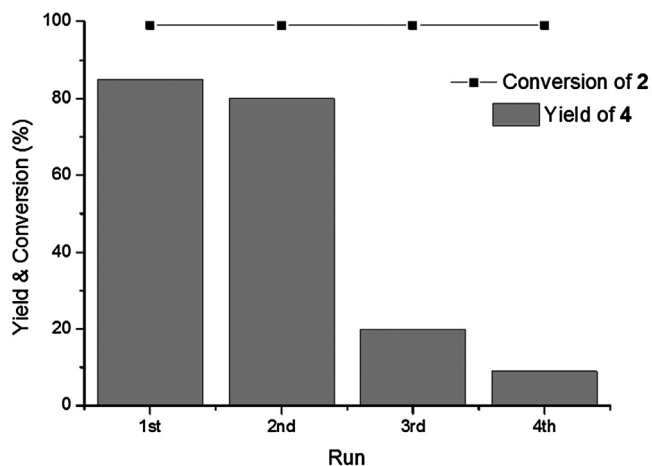


Fig. 2. Main results from the catalyst recycling experiments conducted in *n*-octane with 2 as a substrate.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2017.01.017>.

References

- [1] J.-P. Lange, *Biofuels. Bioprod. Biorefining* 1 (2007) 39–48.
- [2] Y. Roman-Leshkov, J.N. Chheda, J.A. Dumesic, *Science* 312 (2006) 1933–1937.
- [3] J.N. Chheda, Y. Román-Leshkov, J.A. Dumesic, *Green Chem.* 9 (2007) 342–350.
- [4] A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, *Green Chem.* 13 (2011) 754–793.
- [5] J.-P. Lange, E. van der Heide, J. van Buijtenen, R. Price, *ChemSusChem* 5 (2012) 150–166.
- [6] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith Jr., *Green Chem.* 10 (2008) 799–805.
- [7] C. Li, Z. Zhang, Z.K. Zhao, *Tetrahedron Lett.* 50 (2009) 5403–5405.
- [8] P. Wrigstedt, J. Keskiaväli, T. Repo, *RSC Adv.* 6 (2016) 18973–18979.
- [9] F.K. Kazi, A.D. Patel, J.C. Serrano-Ruiz, J.A. Dumesic, R.P. Anex, *Chem. Eng. J.* 169 (2011) 329–338.
- [10] S. De, B. Saha, R. Luque, *Bioresour. Technol.* 178 (2015) 108–118.
- [11] E. Furimsky, *Appl. Catal. A Gen.* 199 (2000) 147–190.
- [12] Q. Bu, H. Lei, A.H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang, R. Ruan, *Bioresour. Technol.* 124 (2012) 470–477.
- [13] G.W. Huber, J. Chheda, C.B. Barrett, J.A. Dumesic, *Science* 308 (2005) 1446–1450.
- [14] J. Yang, N. Li, G. Li, W. Wang, A. Wang, X. Wang, Y. Cong, T. Zhang, *ChemSusChem* 6 (2013) 1149–1152.
- [15] A.D. Sutton, F.D. Waldie, R. Wu, M. Schlaf, L.A. Silks, J.C. Gordon, *Nat. Chem.* 5 (2013) 428–432.
- [16] G. Li, N. Li, J. Yang, L. Li, A. Wang, X. Wang, Y. Cong, T. Zhang, *Green Chem.* 16 (2014) 594–599.
- [17] C.R. Waidmann, A.W. Pierpont, E.R. Batista, J.C. Gordon, R.L. Martin, R.M. West, R. Wu, *Catal. Sci. Technol.* 3 (2013) 106–115.
- [18] Q.N. Xia, Q. Cuan, X.H. Liu, X.Q. Gong, G.Z. Lu, Y.Q. Wang, *Angew. Chemie Int. Ed.* 53 (2014) 9755–9760.
- [19] H.J. Song, J. Deng, M.S. Cui, X.L. Li, X.X. Liu, R. Zhu, W.P. Wu, Y. Fu, *ChemSusChem* 8 (2015) 4250–4255.
- [20] S. Sitthitha, D.E. Resasco, *Catal. Lett.* 141 (2011) 784–791.
- [21] Z. Li, R.S. Assary, A.C. Atesin, L.A. Curtiss, T.J. Marks, *J. Am. Chem. Soc.* 136 (2014) 104–107.
- [22] J. Watson, *Ind. Eng. Chem. Prod. Res. Dev.* 12 (1973) 310–311.
- [23] R. Xing, A.V. Subrahmanyam, H. Olcay, W. Qi, G.P. van Walsum, H. Pendse, G.W. Huber, *Green Chem.* 12 (2010) 1933–1946.
- [24] R.M. West, Z.Y. Liu, M. Peter, C.A. Gärtner, J.A. Dumesic, *J. Mol. Catal. A Chem.* 296 (2008) 18–27.
- [25] W. Shen, G.A. Tompsett, K.D. Hammond, R. Xing, F. Dogan, C.P. Grey, W.C. Conner Jr., S.M. Auerbach, G.W. Huber, *Appl. Catal. A Gen.* 392 (2011) 57–68.
- [26] C.J. Barrett, J.N. Chheda, G.W. Huber, J.A. Dumesic, *Appl. Catal. B Environ.* 66 (2006) 111–118.
- [27] Y. Ni, Z. Sun, *Appl. Microbiol. Biotechnol.* 83 (2009) 415–423.
- [28] K.-H. Lin, A.-N. Ko, *Appl. Catal. A Gen.* 147 (1996) L259–L265.
- [29] E.-S. Kang, D.W. Chae, B. Kim, Y.G. Kim, *J. Ind. Eng. Chem.* 18 (2012) 174–177.
- [30] S. Subbiah, S.P. Simeonov, J.M.S.S. Esperança, L.P.N. Rebelo, C.A.M. Afonso, *Green Chem.* 15 (2013) 2849–2853.
- [31] A.G.M. Barrett, D.C. Braddock, *Chem. Commun.* 10 (1997) 351–352.
- [32] A.E. King, T.J. Brooks, Y.-H. Tian, E.R. Batista, A.D. Sutton, *ACS Catal.* 5 (2015) 1223–1226.
- [33] T.L. Lohr, Z. Li, R.S. Assary, L.A. Curtiss, T.J. Marks, *Energy Environ. Sci.* 9 (2016) 550–564.
- [34] M. Lancaster, *Green Chemistry: An Introductory Text*, Third, The Royal Society of Chemistry, Cambridge, 2016.
- [35] K. Mikami, M. Terada, H. Matsuzawa, *Angew. Chem. Int. Ed. Engl.* 41 (2002) 3554–3572.
- [36] K. Chen, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, *ChemCatChem* 2 (2010) 547–555.
- [37] Y. Nakagawa, K. Tomishige, *Catal. Today* 195 (2012) 136–143.
- [38] K. Chen, K. Mori, H. Watanabe, Y. Nakagawa, K. Tomishige, *J. Catal.* 294 (2012) 171–183.
- [39] R. Bansal, *Organic Reaction Mechanisms*, Third, Tata McGraw-Hill Publishing Company Limited, New Delhi, 1998.
- [40] T.L. Lohr, Z. Li, T.J. Marks, *ACS Catal.* 5 (2015) 7004–7007.
- [41] J. Julis, W. Leitner, *Angew. Chemie Int. Ed.* 51 (2012) 8615–8619.