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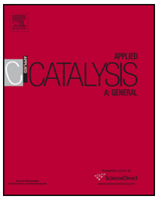

Feature Article

One-step Pd/C and Eu(OTf)$_3$ catalyzed hydrodeoxygenation of branched C_{11} and C_{12} 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 C_{11} and C_{12} 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.

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].

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 C_{11} and C_{12} 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,

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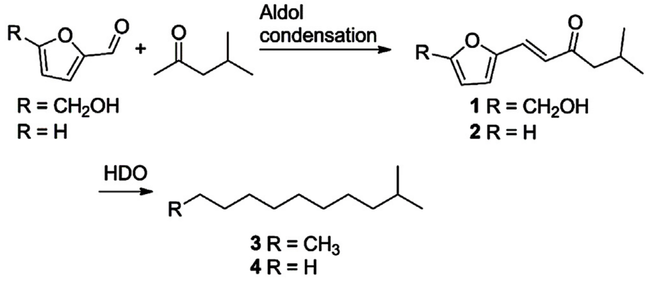

Scheme 1. The high yield two-step procedure from biomass-based furans to branched C_{11} and C_{12} alkanes.

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 (≥98%), HMF (99%) Sigma Aldrich), MIBK (≥98.5% Sigma Aldrich) and base catalyst (NaOH (≥98%), KOH (90%) and K_2CO_3 (99%) Sigma Aldrich, Na_2CO_3 (≥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 × 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 glass insert with magnetic stirring bar. After this, appropriate amount of solvent, cocatalyst (HOTf (≥99%), $Eu(OTf)_3$ (98%), $YbCl_3$ (99.9%), $Nd(OTf)_3$ (98%), $FeCl_3$ (97%) Sigma Aldrich; $Hf(OTf)_4$ (98%), $Fe(OTf)_3$ (90% tech.), $EuCl_3$ (99.9%), $Sc(OTf)_3$ (98%), $Y(OTf)_3$, $LaCl_3$ (99.9%) and $La(OTf)_3$ (99%) Alfa Aesar; $InCl_3$ (98%) Fluka; and $AlCl_3$ (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 30 S). The autoclave was pressurized with H_2 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 (≥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-ZrO_2 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 C_{12} and C_{11} 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 & ^{13}C 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 H_2-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 H_2-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