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An overview of dehydration, aldol-condensation and hydrogenation processes for production of liquid alkanes from biomass-derived carbohydrates

Juben N. Chheda, James A. Dumesic *

University of Wisconsin-Madison, Department of Chemical and Biological Engineering, Madison, WI 53706, USA

Abstract

We present results for the conversion of carbohydrate feedstocks to liquid alkanes by the combination of dehydration, aldol-condensation/hydrogenation, and dehydration/hydrogenation processing. With respect to the first dehydration step, we demonstrate that HMF can be produced in good selectivity from abundantly available polysaccharides (such as inulin, sucrose) containing fructose monomer units using a biphasic batch reactor system. The reaction system can be optimized to achieve good yields to 5-hydroxymethylfurfural (HMF) from fructose by varying the contents of aqueous-phase modifiers such as dimethylsulfoxide (DMSO) and 1-methyl-2-pyrrolidinone (NMP). Regarding the aldol-condensation/hydrogenation step, we present the development of stable, solid base catalysts in aqueous environments. We address the effects of various reaction parameters such as the molar ratio of reactants and temperature on overall product yield for sequential aldol-condensation and hydrogenation steps. Overall, our results show that it is technically possible to convert carbohydrate feedstocks to produce liquid alkanes by the combination of dehydration, aldol-condensation/hydrogenation, and dehydration/hydrogenation processing; however, further optimization of these processes is required to decrease the overall number of separate steps (and reactors) required in this conversion.

Keywords: Bio-fuels; Renewable energy; Aqueous-phase processing; Carbohydrates; Dehydration; Aldol-condensation

1. Introduction

In the view of declining petroleum resources and rising oil prices, it is necessary to develop alternative ways to fulfill the energy needs of our industrialized society. To meet the growing demand for energy, biomass can serve as a sustainable source of renewable fuels and chemicals. In addition to domestic availability, fuels developed from biomass resources are CO_2-neutral, because CO_2 released during combustion can be utilized for biomass growth in the next cycle. A recent report from the U.S. Department of Agriculture (USDA) and U.S. Department of Energy (DOE) estimates that a sustainable production of 1.3 billion dry tonnes of biomass per year can be achieved without significant changes in agricultural practices and food supplies, leading to 20% replacement of transportation fuel demand by 2030 [1]. The primary routes for conversion of biomass to liquid fuels include thermochemical gasification to produce synthesis gas [2], liquefaction of biomass and/or pyrolysis to bio-oils [3], conversion of sugars to ethanol and aromatic hydrocarbons [4,5], and esterification of triglycerides to form bio-diesel [2]. However, development of new technologies is critical to accelerate the development of renewable fuels from biomass. In this respect, the most effective and efficient utilization of renewable biomass resources is through the development of an integrated biorefinery, in which the energy requirements of each process are balanced with those of other processes analogous to petroleum refinery.

Recently, we have developed a process to convert sugar alcohols (e.g., sorbitol) to lighter alkanes (C_1–C_6) using a bifunctional metal-acid (Pt/SiO_2–Al_2O_3) catalyst [6]. The alkanes produced in this process contain 90% of the heating value of glucose and H_2 feed but only 30% of its mass. However, the alkanes produced in this process contain the same number of carbon atoms as the initial sugar (usually 5 or 6 carbon atoms), and hence they cannot be used for fuel

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* Corresponding author. Fax: +1 608 262 5434.
E-mail address: dumesic@engr.wisc.edu (J.A. Dumesic).

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applications due to their high volatility. As a result, we more recently developed a process that produces liquid alkanes, ranging from C_7 to C_{15}, by aqueous-phase processing of biomass-derived carbohydrates, thereby providing a renewable source for transportation fuel [7]. This process can complement the development of P-series fuel (a mixture of approximately equal volumes of ethanol, methyltetrahydrofuran and pentane-plus components) that has over 60% of its current composition resulting from renewable sources [8]. Specifically, the pentane-plus components of this fuel, which are currently derived from petroleum, can be replaced by the lighter alkanes (C_5–C_9) produced from this technology. Moreover, the oxygenated form of saturated organic molecules or heavier liquid alkanes (C_{13}–C_{15}) from our process can serve as diesel-fuel additives. In addition, our process has an overall energy efficiency of 2.1 (ratio of heating value of alkanes to energy required to produce alkanes) as compared to bio-ethanol, which has an energy efficiency of about 1.1–1.3 [9].

As depicted in Fig. 1, the production of heavier liquid phase alkanes from carbohydrates involves a series of reaction steps starting with acid hydrolysis of polysaccharides to produce monosaccharides, followed by acid-catalyzed dehydration to form carbonyl-containing furan compounds such as 5-hydroxymethylfurfural (HMF) and furfural. Subsequently, these compounds can be condensed via aldol reaction to produce larger organic molecules (>C_6) by forming C–C bonds, and these aldol-products can be hydrogenated to form large water-soluble organic compounds. These molecules are then converted to liquid alkanes (ranging from C_7 to C_{15}) by aqueous-phase dehydration/hydrogenation (APD/H) over a bifunctional catalyst containing acid and metal sites in a flow reactor. Thus, dehydration of carbohydrates to produce furanic compounds and the aldol-condensation reaction play important roles in multi-step catalytic production for liquid alkanes. In this work, we address further developments in the dehydration and the aldol-condensation aspects of the above-mentioned process to produce liquid alkanes. In particular, we demonstrate that HMF can be produced in good selectivity from abundantly available polysaccharides (such as inulin, sucrose) containing fructose monomer units using a biphasic batch reactor system. The reaction system is initially optimized to achieve good HMF yields from fructose by varying contents of aqueous-phase modifiers such as dimethylsulfoxide (DMSO) and 1-methyl-2-pyrrolidinone (NMP). We further present the development of stable, solid base catalysts for aldol-condensation in the aqueous phase. We address the effects of various reaction parameters such as the molar ratio of reactants and temperature on overall yield for aldol-condensation combined with the sequential hydrogenation step. The aqueous dehydration/hydrogenation process to produce liquid alkanes is reviewed elsewhere [6,7,9]. Finally, we elucidate the effects of various reaction parameters for each of the processes involved in the conversion of sugars to liquid alkanes, and we present various opportunities to move this technology toward practical application.

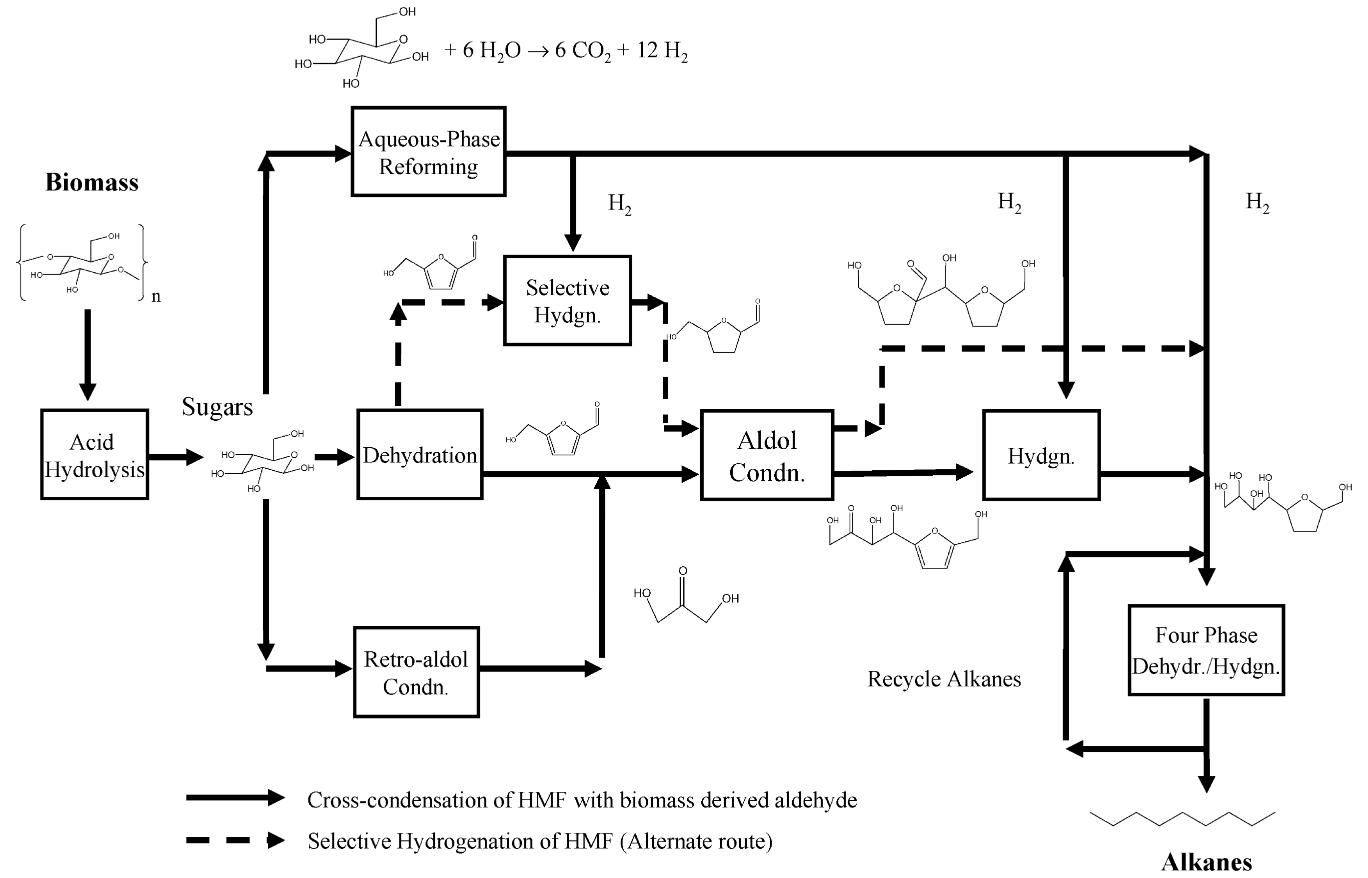

Fig. 1. Schematic diagram for production of liquid alkanes from biomass resources in a biorefinery.

2. State-of-the-art

Dehydration of carbohydrates leads to formation of furan compounds such as furfural and HMF, which are essential intermediates for production of liquid alkanes. While furfural is produced industrially using the Quaker oats technology [10], the large-scale production of HMF is impeded by lack of a cost-effective preparation method [11]. HMF production from fructose and glucose has been performed in water, organic solvents (DMSO) [12] and biphasic systems (water–MIBK) [13] using acid catalysts such as mineral acids (HCl, H_2SO_4) [14], solid acids (zeolites [13], ion-exhange resins [15]) and salts ($LaCl_3$) [16]. Dehydration of fructose to HMF in water is generally non-selective, while high yields (>90%) are obtained in the presence of aprotic solvents such as DMSO [12,17–19]. However, product isolation from high boiling solvents such as DMSO leads to thermal degradation of the HMF product, thereby leading to energy intensive purification procedures. It is known that fructose dehydration to HMF has higher reaction rates and selectivities compared to glucose conversion, even though glucose is the most inexpensive and abundantly available feedstock. In pure water, glucose dehydration is non-selective (6%) [16], while in pure DMSO the maximum HMF yield obtained is 42% at low concentrations (3 wt%) [18]. Similarly, other carbonyl compounds such as dihydroxyacetone and glyceraldehydes can be obtained from retro-aldol-condensation of glucose [20], and acetone can be produced from the fermentation of glucose [2].

Aldol-condensation is generally carried out in the presence of base catalysts to form a carbon–carbon bond between two carbonyl-containing compounds. Among the solid base catalysts that are active for aldol-condensation are alkali and alkaline earth oxides [21–24], phosphates [25], MCM41 [26], and hydrotalcites [27,28]. Aldol-condensation using solid base catalysts has been reported in organic liquid phases or in the vapor phase. Rehydrated forms of hydrotalcite-like catalysts have been shown to be active and stable base catalysts for aldol-condensation in organic media. Base catalysts such as magnesia–zirconia and magnesia–titania have been tested for vapor phase condensation of acetone [29,30]. However, few studies have been reported for aldol-condensation using solid base catalysts in water, because leaching of catalyst components into the water phase and poor hydrothermal stability pose significant challenges. Aldol-condensation in the aqueous environment for carbohydrate-derived molecules has been reported using homogeneous mineral bases such as NaOH [23,31]. Similarly, cross-condensation of furfural with acetone, an important reaction for this process, has been performed previously using amino-functionalized mesoporous base [26] as well as chiral L-proline [32] catalysts in organic solvents.

The subsequent step after aldol-condensation is hydrogenation of aldol-adducts to increase their solubility in the aqueous phase. In addition, selective hydrogenation of the furan ring in HMF and furfural can lead to additional carbonyl-containing compounds that can undergo aldol self-condensation to form heavier alkanes. Thermodynamic considerations favor hydrogenation of the C=C bond over the C=O bond for hydrogenation reactions involving unsaturated aldehydes [33]. Reaction kinetics considerations also favor hydrogenation of the C=C bond over the C=O bond for small molecules [34,35], whereas steric constraints for larger molecules decrease the rates for hydrogenation of C=C bonds. Accordingly, the C=C bonds of furfural are less reactive than the C=O bond, probably due to steric effects [36], making the production of tetrahydrofurfural (THF2A) by hydrogenation of furfural difficult. It has also been reported that Pd exhibits a low rate for hydrogenating the C=O bond compared with other metals commonly used for hydrogenation [34]. Similarly, the aldol-condensation and subsequent hydrogenation using a bifunctional metal-base catalyst has been conducted in the organic phase for production of MIBK [37] and synthesis of α-alkylated nitriles [38] with carbonyl compounds using Pd on hydrotalcites.

3. Production of liquid alkanes from carbohydrates

Fig. 1 shows a schematic diagram for conversion of biomass into liquid alkane fuels, based on aldol-condensation followed by dehydration/hydrogenation. In the first step, polysaccharides such as cellulose, hemicellulose, starch, inulin, etc., are converted to monosaccharides such as xylose, glucose and fructose. Pentoses and hexoses thus formed are converted to carbonyl-containing compounds such as furfural and HMF, respectively, using acid-catalyzed dehydration. The xylose and glucose can also be converted to H_2 for use in subsequent steps by aqueous-phase reforming (APR) [39]. In addition, sugars can be converted to smaller carbonyl compounds such as glyceraldehydes or dihydroxyacetone by retro-aldol-condensation, which can subsequently be used for cross-condensation reactions with HMF or furfural. Similarly, sugars can be fermented to produce acetone that can be cross-condensed with HMF or furfural to form large organic molecules ranging from C_7 to C_{15}. The cross-condensed molecules are then hydrogenated to increase their solubility in the aqueous phase, and these compounds are then fed to a four-phase dehydration/hydrogenation reactor to produce liquid alkanes. Another possible route is to convert HMF and furfural to 5-hydroxymethyl-tetrahydrofurfural (HMTHFA) and tetrahydrofurfural (THF2A), respectively, by (i) selective hydrogenation of the C=C bonds in the five-member rings, (ii) complete hydrogenation of these compounds followed by preferential dehydrogenation of the primary –C–OH group to form an aldehyde (taking advantage of the favorable thermodynamics for this process compared to dehydrogenation of C=C bonds at temperatures near 520–570 K), or (iii) complete hydrogenation followed by selective oxidation of the primary –C–OH group upon reaction with O_2 to form an aldehyde. The HMTHFA and THF2A are then self-condensed to form C_{12} species that are subsequently hydrogenated to form water-soluble organic species. The four-phase dehydration/hydrogenation reactor system consists of (i) an aqueous inlet stream containing large water-soluble molecules, (ii) a hexadecane alkane sweep inlet stream, (iii) a H_2 inlet gas stream, and (iv) a solid catalyst (Pt/SiO_2–Al_2O_3) [7]. As dehydration/hydrogenation takes place the aqueous organic reactants become more hydrophobic, and the hexadecane alkane stream serves to remove hydrophobic species from the catalyst before they react further to form coke. Essentially, the intermediate steps for conversion of biomass to liquid alkane fuels involve changing the functionality of the sugars through a series of selective reactions including dehydration, hydrogenation/dehydrogenation, and oxidation, followed by changing the molecular weight through aldol-condensation and subsequently hydrogenating the aldol-adducts to form large water-soluble compounds.

Fig. 2 shows the reaction pathways involved in the production of liquid alkanes from polysaccharides. At first, the hydrolysis reaction involves breaking C–O–C linkages to form simpler carbohydrate molecules, and this process is typically carried out at high temperatures in the presence of mineral acid catalysts. Cellulose, which is the most abundant biomass constituent, is difficult to hydrolyze because of its high degree of crystallinity [40]. In contrast, hemicellulose, a precursor for C_5 sugars, can be hydrolyzed at moderate temperatures using dilute acids [40]. These carbohydrates can subsequently undergo dehydration by loss of three water molecules to form furan compounds such as HMF and furfural. Dehydration reactions are typically carried out in the presence of solid or mineral acid catalysts at moderate temperatures of 373–473 K. Subsequently, aldol-condensation involves the C–C coupling between two compounds containing carbonyl groups to form larger organic molecules. The reaction is carried out in polar solvents such as water or water–methanol in the presence of base catalysts such as mixed Mg–Al-oxides or $MgO–ZrO_2$ at low temperatures. As indicated in Fig. 2, acetone first reacts with HMF to form C_9 species, which can subsequently react with a second HMF molecule to form a C_{15} molecule. The aldol-products have limited solubility in water and they precipitate out of the aqueous phase. The subsequent hydrogenation step saturates the C=C and C=O bonds of the aldol-adducts over a metal catalyst (Pd/Al_2O_3), thereby producing large water-soluble organic compounds. These water-soluble organic molecules subsequently undergo repeated dehydration/hydrogenation reaction in the presence of bifunctional catalysts containing acid and metal sites ($Pt/SiO_2–Al_2O_3$) to form liquid alkanes in a four-phase reactor system. Alternatively, C=C bonds in the furan ring can be selectively hydrogenated to form HMTHFA, which retains the carbonyl group and also contains an α-H to undergo self-condensation to form C_{12} alkanes.

Aldol-condensation is a key intermediate step to form large organic molecules using carbohydrate-derived carbonyl compounds. Even though sugars contain a carbonyl group, they form ring structures in aqueous solution at room temperature resulting in less than 1% of the acyclic form [20]. This behavior leads to low reactivity of sugars for aldol-condensation reaction. In addition, the multiple –OH groups in sugars are highly reactive toward formation of various by-products in alkaline solution. In contrast, it is possible to dehydrate glucose, fructose and xylose to 5-hydroxymethylfurfural (HMF) and furfural, respectively. It is important to note that HMF and furfural cannot undergo self-condensation reactions, because they do not have an α-H atom that is required for the aldol-condensation reaction. However, both HMF and furfural have aldehyde groups that can condense with other molecules that

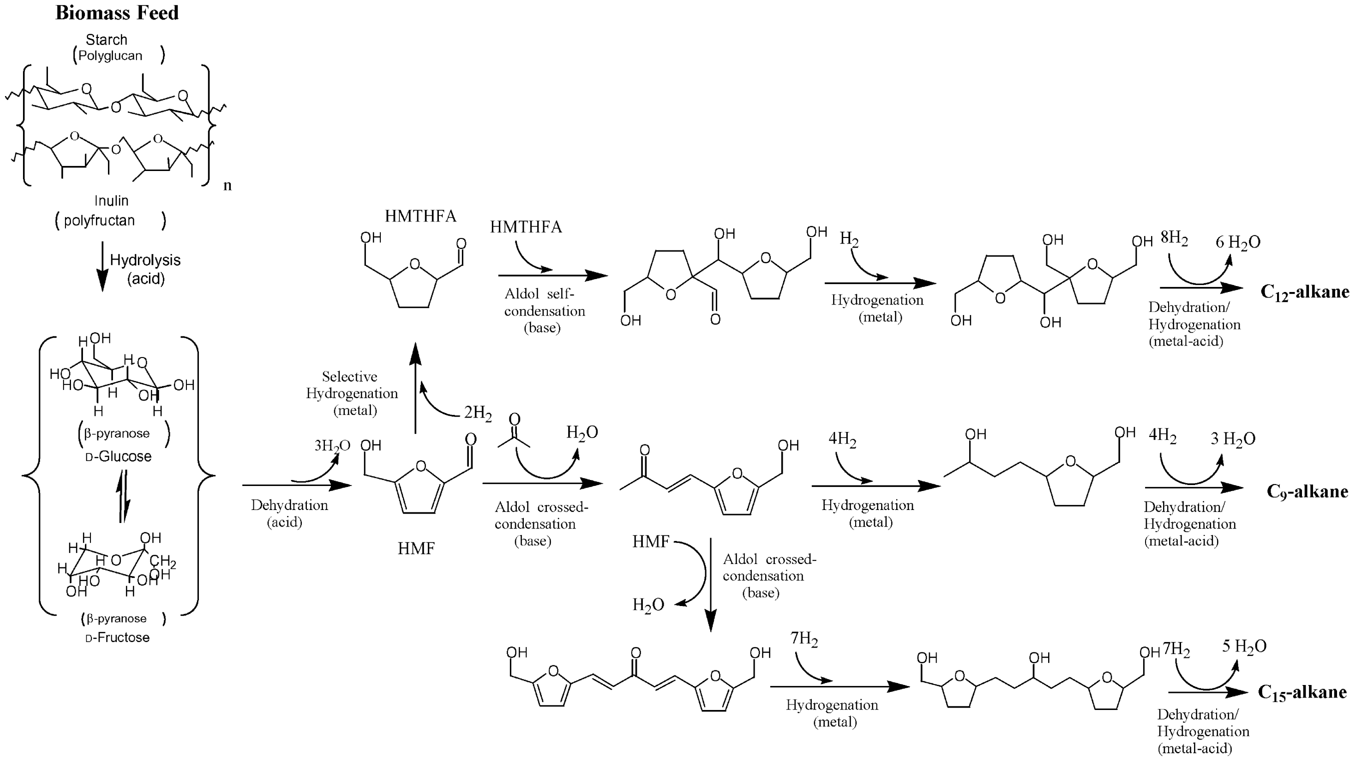

Fig. 2. Reaction pathways for conversion of polysaccharides into liquid alkanes. Analogous chemistry can be depicted for conversion of C_5 polysaccharides to C_{10}, C_8 and C_{13} alkanes, respectively, via furfural as reaction intermediate.

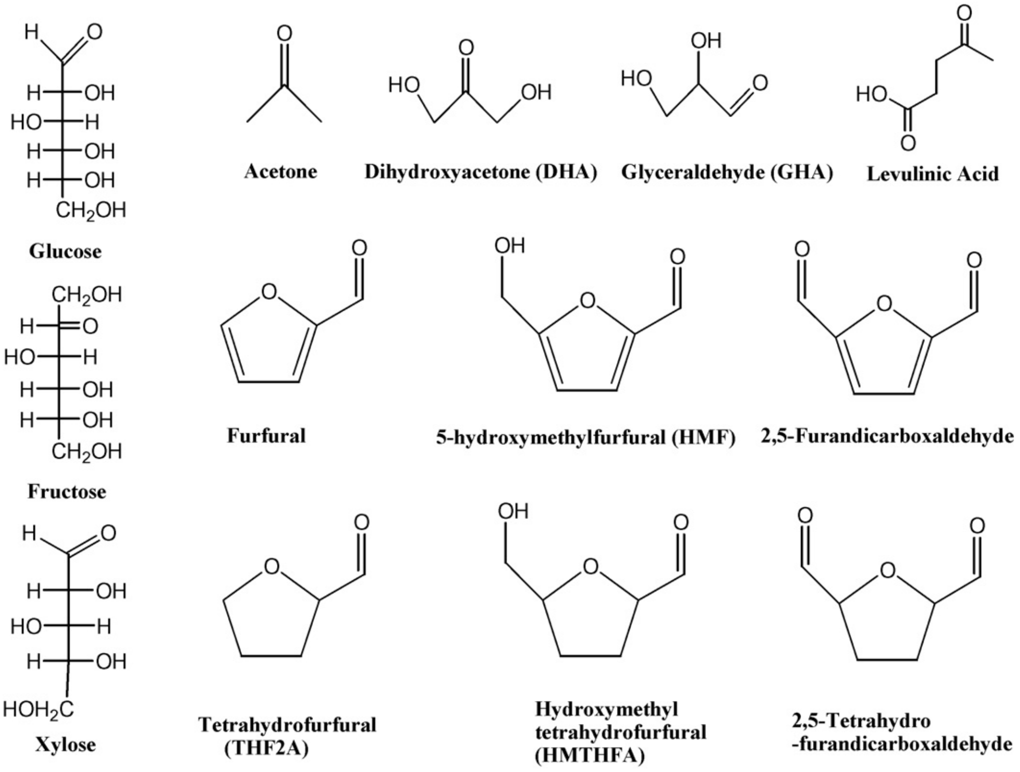

Fig. 3. Carbonyl compounds derived from carbohydrate feedstocks.

can form carbanion species, such as acetone, dihydroxyacetone (DHA) or glyceraldehyde (GHA). Alternatively, if the C=C bonds of HMF and furfural can be selectively hydrogenated to produce HMTHFA and THF2A, respectively, then these species could form a carbanion species and undergo self condensation. In general, Fig. 3 shows a variety of oxygenated carbonyl compounds that can be derived from carbohydrates, and which can potentially be self or cross-condensed to form large organic molecules.

4. Experimental

4.1. Materials and catalysts synthesis

All chemicals including fructose, inulin, sucrose, dichloromethane (DCM), methylisobutylketone (MIBK), acetone, HMF, furfural, DMSO, NMP were purchased from Sigma–Aldrich Inc. Ion-exchange resin (DIAION® PK216) catalysts was purchased from Mithushi Chemicals Corporation. The resin was activated by equilibrating one volume of resin in three volumes of 1N HCl solution for 30 min. The catalyst was then washed with de-ionized water until the filtrate solution was neutral.

Mixed Mg–Al-oxide catalyst with Mg/Al atomic ratio = 2 was prepared by adding $Mg(NO_3)_2\cdot 6H_2O$ (0.188 mol) and $Al(NO_3)_3\cdot 9H_2O$ (0.093 mol) to 200 g of H_2O. A second solution containing NaOH (0.438 mol) and Na_2CO_3 (0.113 mol) in 200 g of H_2O was slowly added to the Mg/Al aqueous solution in a 1000 ml flask with constant stirring over a period of 3 h. All chemicals were purchased from Aldrich. The pH of the solution was maintained at 11.0 by adding additional NaOH solution (25 wt%) when required. This solution was then heated to 338 K for 18 h. A precipitate formed, which was subsequently filtered and washed with de-ionized water until the sodium (Na) content of the filtrate was below 10 ppm as measured by ICP analysis. The precipitate was dried in an oven at 353 K for 12 h to obtain the hydrotalcite. Calcination of the hydrotalcite was carried out in flowing O_2 (GHSV ~400 h^{-1}), during which the temperature was ramped from room temperature to 723 K over 2 h and then held at 723 K for 8 h. The mixed Mg–Al-oxide catalyst thus prepared was used to carry out aldol-condensation reactions.

Magnesia–zirconia (MgO/ZrO_2) and magnesia–titania (MgO/TiO_2) catalysts were synthesized using the sol–gel technique described by Aramendía et al. [39]. A 5 wt% Pd/$MgO–ZrO_2$ catalyst was prepared by incipient wetness impregnation of Pd onto the above-mentioned $MgO–ZrO_2$ support as described in detail by Barrett et al. [41]. Similarly, La/ZrO_2, Y/ZrO_2 and MgO/ZrO_2-I were prepared by incipient wetness impregnation of La, Y and Mg salts on ZrO_2 and activated by calcining for 2 h in flowing O_2 (100 $cm^3\ min^{-1}$) at 723 K. A catalyst consisting of *N*-methyl-3-aminopropylated (NMAP) SiO_2 was prepared using the procedure described by Hamaya et al. [42].

4.2. Reactor system and analysis methods

Dehydration reactions were carried out in a two-phase batch reactor system containing a reactive aqueous layer (mixture of water/DMSO or water/NMP) and an extracting organic layer

Table 1
Results for dehydration of fructose and its precursors (i.e. inulin and sucrose) to HMF

Run	Sugar	Aqueous layer (w/w)	Organic layer	Temperature (K)	Catalyst	Time (h)	Conversion	Selectivity	$[\mathrm{HMF}]_{\mathrm{org}}$ ($\mathrm{g\ cm^{-3}}$)	$[\mathrm{HMF}]_{\mathrm{aq}}$ ($\mathrm{g\ cm^{-3}}$)	R
1	Fructose	W	MIBK	363	Resin	21	60	47	0	0	1.07
2	Fructose	8:2 W:DMSO	MIBK	363	Resin	21	68	60	0.0125	0.0133	0.94
3	Fructose	5:5 W:DMSO	MIBK	363	Resin	12	90	81	0.0169	0.0325	0.52
4	Fructose	3:7 W:DMSO	MIBK	363	Resin	4	87	84	0.0150	0.0367	0.41
5	Fructose	7:3 W:NMP	MIBK	363	Resin	18	77	68	0.0146	0.0221	0.66
6	Fructose	4:6 W:NMP	MIBK	363	Resin	18	98	85	0.0189	0.0383	0.49
7	Fructose	5:5 W:DMSO	MIBK	393	–	24	67	77	0.0119	0.0234	0.51
8	Fructose	5:5 W:DMSO	DCM	393	–	5.5	92	80	0.0313	0.0314	1.00
9	Fructose[a]	5:5 W:DMSO	MIBK	393	–	21	75	71	0.0257	0.0451	0.57
10	Inulin	5:5 W:DMSO	MIBK	363	Resin	21	100	62	0.0158	0.0304	0.52
11	Inulin	4:6 W:NMP	MIBK	363	Resin	21	100	69	0.0202	0.0313	0.65
12	Inulin	5:5 W:DMSO	DCM	393	–	6.5	100	61	0.0301	0.0266	1.13
13	Sucrose[b]	5:5 W:DMSO	MIBK	363	Resin	21	55	69	0.0094	0.0172	0.55
14	Sucrose[b]	4:6 W:NMP	MIBK	363	Resin	21	58	74	0.0125	0.0176	0.71
15	Sucrose[b]	5:5 W:DMSO	DCM	393	–	6.5	60	69	0.0195	0.0166	1.17

All runs were carried with 10 wt% feed concentration, except run 9 that was carried out with 20 wt% fructose concentration. For all runs, equal amount by weight of organic solvent was used as compared to aqueous phase. Organic/catalyst ratio of 1 was used for all the catalyst runs. $R = [\mathrm{HMF}]_{\mathrm{aq}}/[\mathrm{HMF}]_{\mathrm{org}}$.

[a] 20 wt% fructose feed concentration.

[b] HMF selectivity is based on fructose content.

(MIBK or dichloromethane). Dehydration experiments using MIBK as the extracting phase were carried out in 25 ml (Alltech) glass reactors heated in a temperature-controlled oil bath placed on a magnetic stirrer. The temperature in the oil bath was measured by a K-type thermocouple (OMEGA), and temperature was controlled using a series 16 A controller (Dwyer Instruments) coupled with a 150 W heating cartridge (McMaster Carr). In a typical experiment, 5 g of aqueous-phase solution and 5 g of organic phase solution were poured into the reactor along with ion-exchange resin (organic/catalyst ratio of 1). The reactor was placed in an oil bath at 363 or 393 K for the time specified in Table 1. The reaction was stopped by cooling the reactor to room temperature by flowing air. In a typical run with dichloromethane (DCM) as the extracting solvent, a Parr reactor (Model # 4749, size 23 ml) was filled with 7 g of the sugar aqueous solution and 7 g of dichloromethane. The Parr reactor was then immersed in an oil bath at 393 K for the times indicated in Table 1. After reaction, the reactor was cooled to room temperature by flowing air.

After each dehydration run, portions of the aqueous and organic phases were pipetted out and analyzed using HPLC analysis in a Waters 2690 system equipped with PDA 960 UV and RI 410 refractive index detectors. Sugar disappearance was monitored with an Aminex HPX-87H column (Bio-Rad), using Milli-Q water (pH 2) as the mobile phase at a flow rate of 0.6 ml/min and a column temperature of 303 K. HMF was quantified in the aqueous and organic phases with a Zorbax SB-C18 reverse phase column (Agilent), using a 2:8 (v/v) methanol:water (pH 2) gradient at a flow rate of 0.7 ml/min and a column temperature of 303 K using a UV detector (320 nm). Volumes of each phase after mixing were measured using standard solutions for sugar conversion and HMF selectivity calculations.

Experiments were conducted to test the stabilities of various base catalysts for the condensation of HMF with acetone (molar ratio of 1:10) in 50 ml glass reactor vessels using an oil bath to control the reaction temperature. The runs with mixed Mg–Al-oxides were carried out at room temperature, whereas the runs with the other catalysts were carried out at 323 K. Samples were withdrawn, filtered, and the HMF disappearance was analyzed by HPLC, as described above.

5. Selective dehydration of fructose and its precursors to HMF

Hexoses can undergo dehydration reaction by loss of three water molecules to form 5-hydroxymethylfurfural (HMF) over an acid catalyst. Fructose dehydration to HMF proceeds through open chain 1,2-enediol transformation [13] or through cyclic fructofuransyl pathways [43–45]. In parallel, the reaction intermediates and the HMF product can degrade further to various by-products via fragmentation, condensation, rehydration, reversion and/or additional dehydration reactions. In a biphasic reactor system (Fig. 4), fructose dehydrates in presence of an acid catalyst in the reactive aqueous phase, and the HMF product is continuously separated into the organic extracting phase, thereby decreasing loss of the HMF product toward formation of by-products.

We conducted fructose dehydration experiments in the presence of ion-exchange resin catalyst at 363 K in a biphasic system using a reactive aqueous-phase modified by an aprotic solvent, such as DMSO, and using MIBK as an extracting solvent. Initially, the DMSO content was varied from 0 to 70% in the aqueous phase to study the effect on HMF selectivity from fructose dehydration. Fig. 5 shows that increasing the DMSO content to 50% increased the selectivity from 47 to 81% and doubled the dehydration rate (Table 1, runs 1–3). Previous studies have shown that DMSO suppresses both the formation of condensation by-products and the HMF rehydration to levulinic acid by lowering the overall water concentration

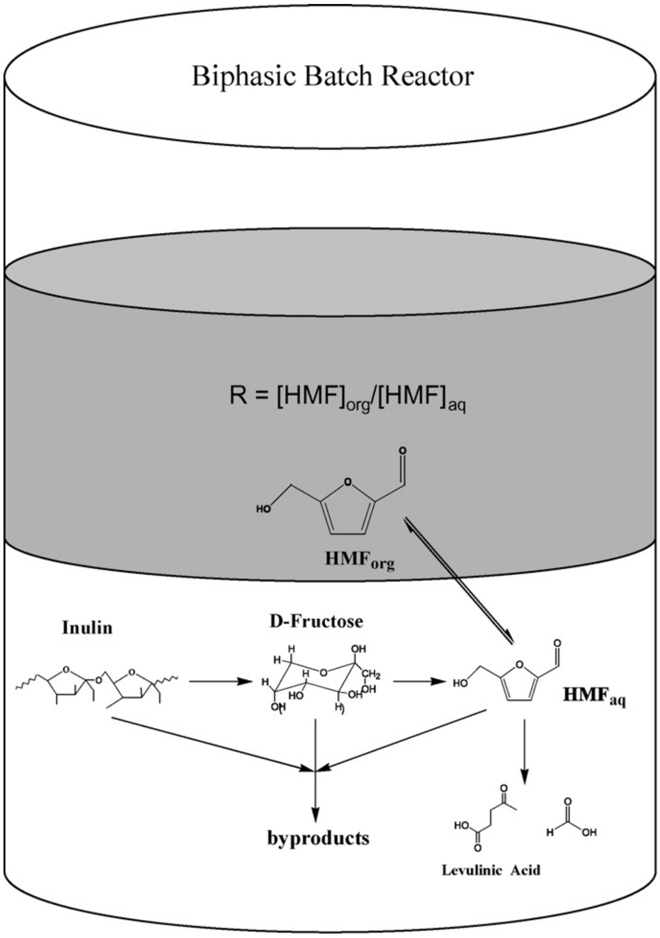

Fig. 4. Batch process for production of HMF from inulin (polyfructan). The aqueous phase contains inulin, DMSO or NMP, and the acid catalyst, and this phase is represented in the bottom half of the batch reactor. The organic phase (gray) contains MIBK or dichloromethane (DCM), and this phase is represented in the top half of the batch reactor.

[11,19]. It is also known that DMSO favorably shifts the equilibrium of the rate-determining step by increasing the furanose form in HMF production, and DMSO inhibits acyclic reaction sequences that lead to undesirable products [46–48]. Further increasing the DMSO content to 70% increased the selectivity by only 3%; however, it results in a corresponding decrease in the extracting power of the organic solvent, as indicated by a decrease in value of the extraction ratio, R (defined as ratio of HMF concentration in the organic layer to that in the aqueous layer), from 1.07 to 0.41 (Table 1, runs 1–4). In addition, a higher fraction of DMSO is carried over to the extracting phase in 3/7 (w/w) W:DMSO (∼5 wt%) as compared to 5/5 (w/w) W:DMSO (∼1.5 wt%) resulting in a compromise between selectivity improvement and added energy expense in HMF product isolation due to DMSO carry-over to the organic phase. Similar effects were observed in presence of another aprotic modifier such as NMP, thereby increasing the HMF selectivity to 85% at 60 wt% level (Table 1, runs 1, 5, 6). However, NMP has a higher carry-over to the organic phase as compared to DMSO, thereby complicating the HMF separation procedure.

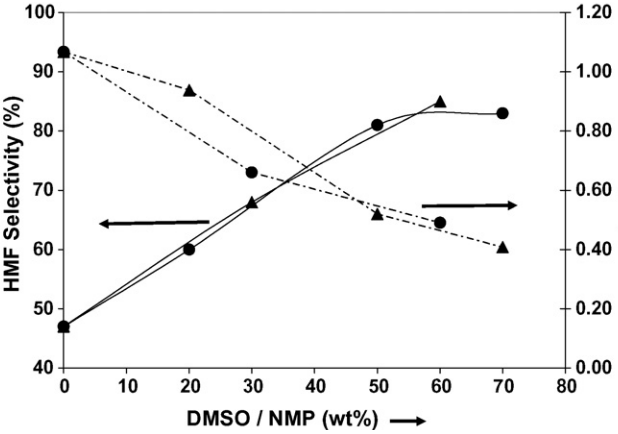

Fig. 5. Effect of adding DMSO and NMP (wt%) in water on HMF selectivity (left axis) and extracting ratio R (right axis) from fructose dehydration. $R = [HMF]_{org}/[HMF]_{aq}$. solid circles, DMSO; solid triangles, NMP.

In further experiments, it was found that the dehydration reaction can be carried out without any catalyst in the presence of 5/5 (w/w) W:DMSO at 393 K, with a selectivity of about 77% (Table 1, run 7). This finding not only eliminates the cost of catalyst but it also eliminates catalyst deactivation problems caused by the formation of insoluble by-products during dehydration processes. Subsequently, we studied the effect of changing the extracting solvent to dichloromethane (DCM) at 393 K. In the presence of DCM as extracting solvent, the reaction rates improved four times while still achieving 80% HMF selectivity (Table 1, run 8). However, DMSO carry-over in dichloromethane was about 8.5 wt% as compared to 1.5 wt% in the presence of MIBK, thereby increasing subsequent separation cost. Similarly, increasing the fructose feed concentration to 20 wt% in the 5/5 (w/w) W:DMSO-MIBK reaction system resulted in a decrease of HMF selectivity to 71% (Table 1, run 9), possibly due to higher rates of condensation reactions.

We recently showed that using the biphasic reactor system, fructose can be dehydrated in the aqueous phase using a mineral acid catalyst (HCl) in high yields (80% selectivity at 90% conversion) at high concentrations (10–50 wt%) when polar aprotic molecules such as DMSO and poly(1-vinyl-2-pyrrolidinone) (PVP) are added in the aqueous phase to suppress undesired side reactions [49]. The reaction rates are considerably higher under these conditions due to presence of mineral acid as well as high temperatures (453 K). The HMF product is extracted continuously into an organic phase (MIBK) modified with 2-butanol to enhance the partitioning of HMF from the reactive aqueous solution, thereby providing a highly efficient method for HMF synthesis from fructose. Importantly, it was found that a hydrophilic polymer such as PVP, which contains the NMP moieties along the polyethylene chain, retains the benefit of selectivity improvement due to the presence of NMP but eliminates the organic phase contamination due to carry-over of NMP into the extracting solvent.

Although, fructose can be processed efficiently by the above-mentioned process, it is important to develop a system that can process abundantly available polysaccharides. Consequently, we

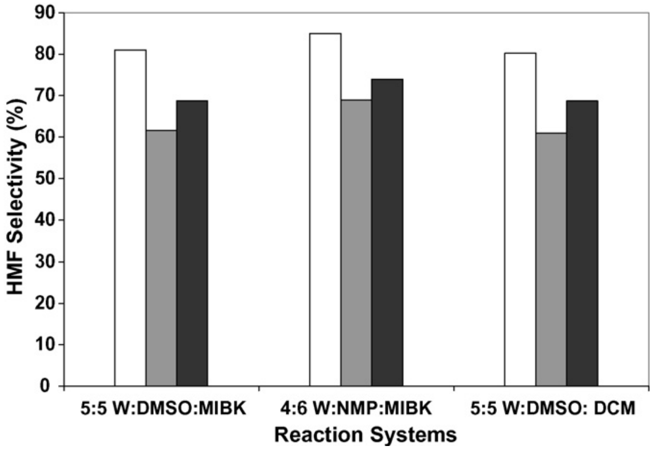

Fig. 6. HMF selectivities from processing of fructose and its precursors (inulin and sucrose) in different reaction systems and conditions. HMF selectivities for sucrose are based on the fructose content of the molecule. White bars represent fructose, gray bars represent inulin and black bars represents sucrose as feed molecules. First system consists of 5:5 W:DMSO as aqueous phase and MIBK as organic phase in the presence ion-exchange resin as catalyst at 363 K. Second system consist of 4:6 W:NMP and MIBK as extracting solvent in the presence of ion-exchange resin as catalyst at 363 K. Third system consists of 5:5 W:DMSO as aqueous phase and DCM as organic phase in the presence of no catalyst at 393 K.

conducted experiments with inulin (a polyfructan obtained from chicory roots) and sucrose (a dimer containing glucose and fructose obtained from cane sugar) using DMSO and NMP as aqueous-phase modifiers with MIBK as the extracting solvent using ion-exchange resin at 363 K. As seen in Fig. 6, inulin can be processed with equally good selectivity as fructose, considering that some losses occur due to hydrolysis of multiple glycosidic C–O–C bonds (Table 1, runs 10 and 11). Similarly, sucrose conversion to HMF based on the fructose half of this molecule shows equally good selectivity as fructose, while leaving the glucose molecules unreacted (Table 1, runs 13 and 14). Similar results were observed when inulin and sucrose were converted using dichloromethane as the extracting solvent at 393 K with no catalyst (Table 1, runs 12 and 15), indicating that polysaccharides can be processed using the biphasic system, thereby eliminating a separate hydrolysis processing step.

6. Aldol-condensation and subsequent hydrogenation to form large water-soluble alkane precursors

Aldol-condensation and subsequent hydrogenation are key intermediate steps to produce large water-soluble organic molecules that can be converted to liquid alkanes by aqueous-phase dehydration/hydrogenation. Base-catalyzed condensation begins with abstraction of α-hydrogen from a nucleophile (such as acetone, DHA, GHA) to form an intermediate carbanion species, which then attacks the carbonyl carbon atom of HMF or furfural to form a C–C bond. Initially, mixed Mg–Al-oxides prepared by hydrotalcite-like syntheses were used to carry out the aldol-condensation reaction at room temperature. As indicated in Fig. 2, reaction between acetone and HMF results in formation of a C_9-species that undergoes dehydration to form an α-β unsaturated C_9 aldol-adduct (monomer). The C_9-monomer can subsequently react with another HMF molecule to form C_{15} species (dimer). These α-β unsaturated aldol products have low solubility in water because of their non-polar structure; hence, they precipitate out of aqueous solution (Fig. 7). Following the aldol-condensation reaction, hydrogen is introduced into the reactor along with a metal catalyst (Pd/Al_2O_3), leading to hydrogenation of the furan rings, thereby increasing the solubility of these molecules in the aqueous phase. The molecular weight distribution of the final alkanes is dictated by the overall yield of aldol-products, which in turn depends on the feed concentration, co-reactant molar ratio, temperature, and the nature of the base catalyst.

We studied the stability of base catalysts in the aqueous environment by conducting recycle runs. It was found that a mixed Mg–Al-oxide catalyst lost approximately 79% and subsequently 96% of its initial activity after the second and third uses, even after calcinations of the catalyst between the recycle runs for the aldol-condensation of HMF with acetone (HMF:acetone molar ratio 1:10). Mixed Mg–Al-oxides catalysts are known to undergo structural and corresponding activity changes in the presence of water, leading to deactivation of the catalysts upon recycling. Afterwards, we tested various base catalysts for recycling ability including MgO, CaO, La/ZrO_2, Y/ZrO_2, MgO/ZrO_2-I (prepared by incipient wetness impregnation), MgO/ZrO_2 (prepared by sol–gel techniques), MgO/TiO_2 and organic catalysts such as *N*-methyl-3-aminopropylated (NMAP) silica. CaO was found to be active for aldol-condensation, but the catalyst leached into aqueous solution. Y/ZrO_2 and La/ZrO_2 showed poor activity even at higher temperatures such as 353 K. A plot of initial activity (Fig. 8A) for various catalysts indicates that MgO/ZrO_2 and MgO/TiO_2 exhibited high activity similar to the most active Mg–Al-oxide catalyst. As indicated in Fig. 8B, consecutive runs with various catalysts indicate that MgO–ZrO_2, MgO–TiO_2 and MgO–ZrO_2–I showed excellent recycling ability upon repeated use for aldol-condensation in the aqueous phase. In fact, ZrO_2 and TiO_2 are known to be stable supports in the aqueous environment. Notably, MgO/ZrO_2–I prepared by impregnating MgO on the ZrO_2 support showed lower activity compared to MgO/ZrO_2 prepared by sol–gel techniques, thereby indicating the effect of preparation technique on the activity of the base catalyst.

In separate experiments, the mixed Mg–Al-oxide catalyst when physically mixed with a Pd/Al_2O_3 hydrogenation catalyst showed a 15% loss of selectivity towards dimer and a 10% loss of overall carbon, thereby indicating a negative effect of Pd/Al_2O_3 on the performance of the base catalyst for aldol-condensation. Because the aldol-product precipitates out of aqueous solution, it is difficult to filter the base catalyst after aldol-condensation. Subsequent addition of metal catalysts for hydrogenation thus leads to catalyst separation problem for recycle runs. Thus, we deposited Pd onto the stable MgO–ZrO_2 catalyst to develop a bi-functional metal-base Pd/MgO–ZrO_2 catalyst [41]. Fig. 9 shows the aqueous-phase concentration of carbon (normalized to the initial concentration of carbon in the batch reactor) versus time during aldol-condensation of HMF:acetone (1:1) carried out in the presence of the

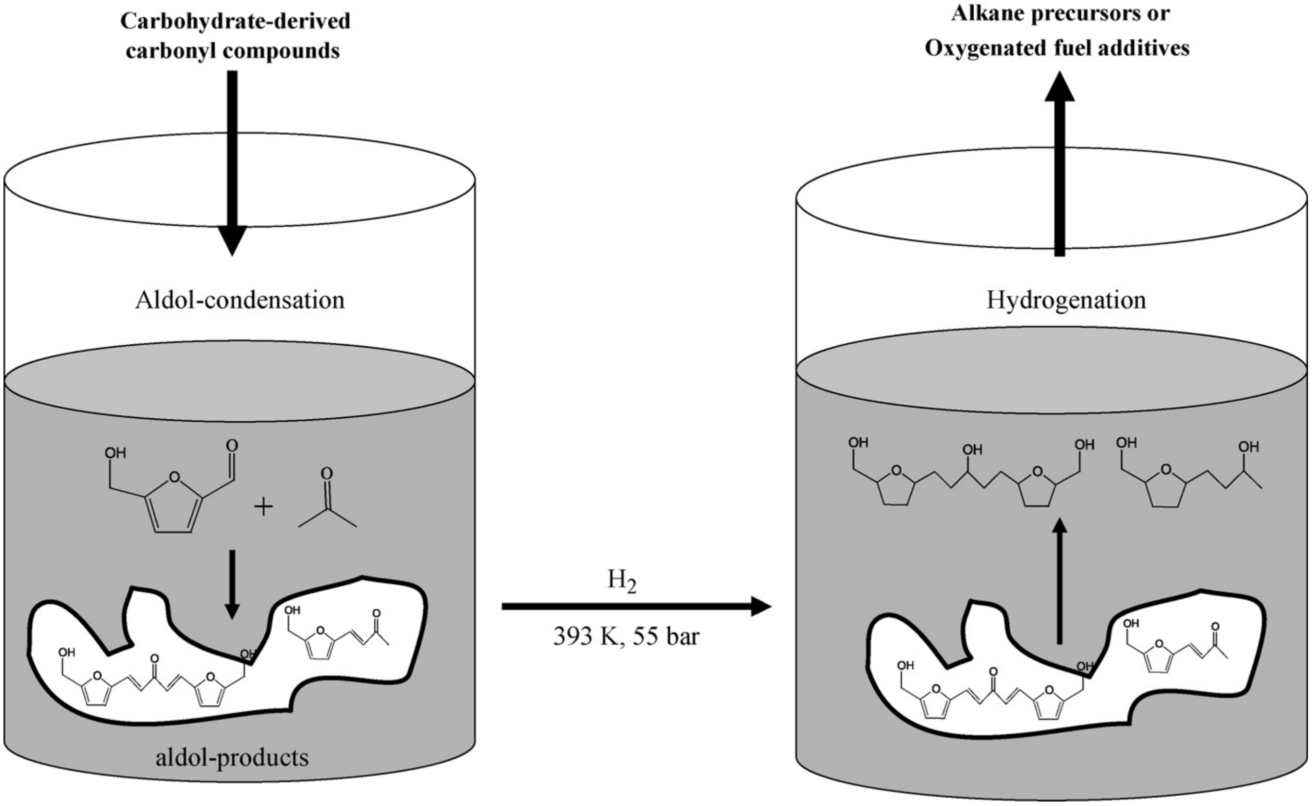

Fig. 7. Batch reactor system for conducting aldol-condensation and sequential hydrogenation of HMF and acetone (molar ratio of 1:1) to form water-soluble oxygenated fuel additives or liquid alkane precursors.

bifunctional catalyst at 326 K followed by hydrogenation in the same batch reactor at 393 K. As aldol-condensation proceeds, the carbon concentration in the aqueous-phase decreases to 44% as the monomer and dimer products precipitate out of the aqueous phase. Hydrogen is subsequently introduced into the reactor to initiate hydrogenation, which leads to an increase in the aqueous-phase carbon concentration to a value of about 94% of the initial carbon in the liquid phase. This example illustrates the ability of the bifunctional Pd/MgO–ZrO$_2$ catalyst to facilitate a single-reactor, aqueous-phase process combining aldol-reaction with sequential hydrogenation, in which the carbon lost during the first step is returned to the aqueous phase during the hydrogenation step. Importantly, the Pd on the catalyst remains inert during aldol-condensation, because the

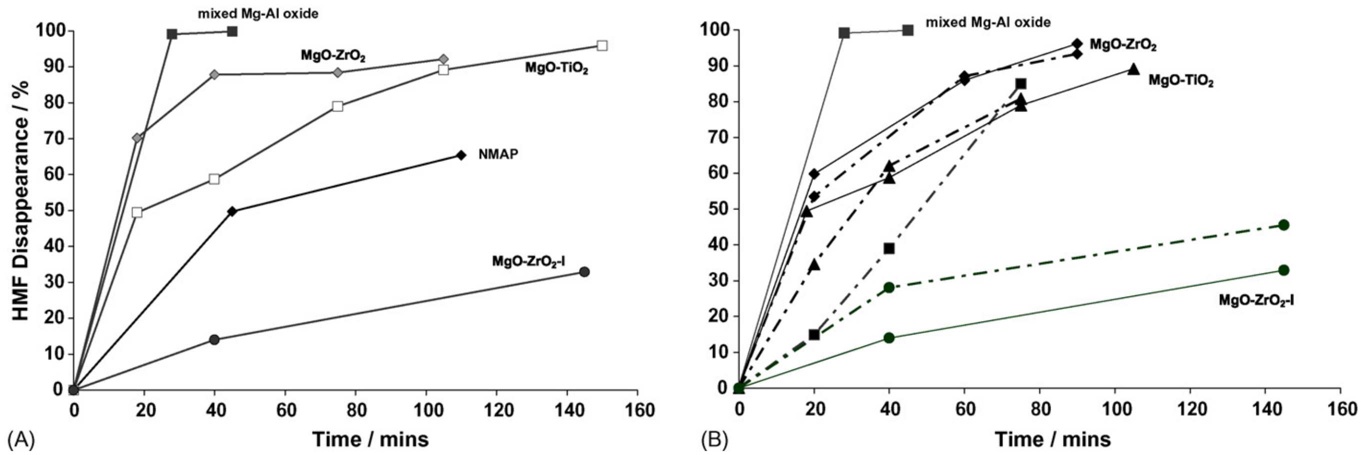

Fig. 8. Effect of various base catalysts on HMF disappearance during aldol-condensation of HMF:acetone (molar ratio of 1:10). (A) Initial activity of various base catalysts for aldol-condensation carried out at 323 K, except for mixed Mg–Al oxide carried out at 298 K. Black squares, mixed Mg–Al-oxides; gray diamonds, MgO–ZrO$_2$; white squares, MgO–TiO$_2$; black diamonds, NMAP SiO$_2$; black circles, MgO–ZrO$_2$–I (prepared by incipient wetness). (B) Recycle runs with various base catalysts for aldol-condensation carried out at 323 K, except for mixed Mg–Al oxide carried out at 298 K. Open lines represent the recycle run 2 conducted after intermediate catalysts regeneration. squares, mixed Mg–Al oxide; diamonds, MgO–ZrO$_2$ (prepared by sol–gel technique); triangles, MgO–TiO$_2$; circles, MgO–ZrO$_2$–I (prepared by incipient wetness).

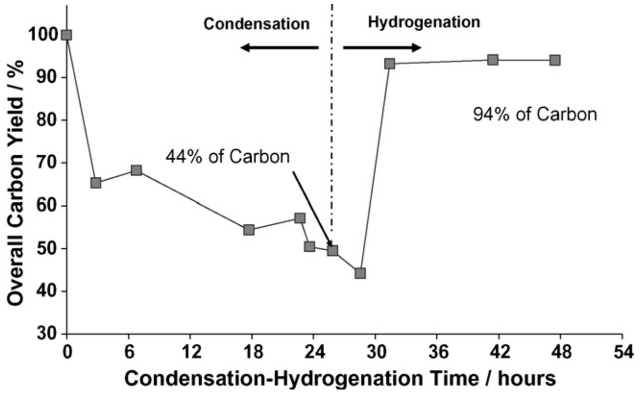

Fig. 9. Overall carbon yield in the aqueous phase vs. time for aldol-condensation at 326 K of HMF with acetone (molar ratio of 1:1) in the presence of 5 wt% Pd/MgO–ZrO_2 catalyst followed by hydrogenation at 393 K. (For detailed reaction conditions and figure adaptation see Ref. [41].)

performance of the bifunctional catalyst was identical to the performance of MgO–ZrO_2 during aldol-condensation. The aldol-condensation runs are not mass transfer limited, as indicated by the Weisz–Prater number (N_{w-p} (acetone) = 0.008, N_{w-p} (furfural) = 0.08 < 0.3) for the aldol-condensation reaction of furfural:acetone (1:1). Further stability runs indicated that the selectivity towards the dimer product decreases by 18% in recycle runs 2 and 3 without intermediate regeneration, but it returns to its original level in recycle run 4, indicating that the catalyst activity can be completely recovered through calcinations [41]. The catalyst retained the number of metal sites (50 μmol/g), surface area (300 m^2/g), and average particle size (∼11 nm) before and after reaction. In addition, MgO and ZrO_2 phases remain unchanged, as shown by XRD measurements, thereby demonstrating the hydrothermal stability and recycling ability of this bifunctional catalyst [41].

In reaction optimization studies, it was found that rate of aldol-condensation increased with increase in temperature, while the overall carbon yield decreased in the aqueous solution due to formation of coke on the catalyst during aldol-condensation [41]. The effects of reaction temperature and molar ratio of reactants were optimized for cross-condensation of acetone with furfural to form C_8 and C_{13} species. Fig. 10A shows that the optimum temperature of the furfural–acetone condensation reaction is about 353 K, as increasing the temperature from 326 to 353 K increases the dimer selectivity by 17% with no significant changes in carbon yield. On the other hand, operating at the higher temperature of 393 K resulted in equivalent selectivity for dimer with a 8% decrease in overall carbon yield. Similar effects of temperature were observed on acetone condensation with HMF resulting in 353 K as the reaction optimum temperature. Fig. 10B demonstrates that the molar ratio of reactants plays a significant role in controlling the selectivity for aldol-condensation. In the presence of excess acetone (molar ratio furfural:acetone 1:9), reaction leads to the formation of C_8 species, because it is more probable that furfural will react with abundant acetone molecules as compared to monomer species. Similarly, increasing the ratio from 1:9 to 1:1 increases the dimer selectivity by 31% with a further increase in selectivity by 12% at molar ratio of 2:1. Varying the palladium loading (from 0.5 to 5 wt%) and the organic/catalyst ratio (from 6 to 36) did not have significant effects on the catalyst activity or selectivity. In a separate experiment, the catalyst and the insoluble monomer and dimer species were separated from the aqueous solution and hydrogenated in hexadecane to recover 71% of the carbon, thereby indicating that hydrogenated form of monomer and dimer can be blended with diesel fuel without the need to convert to liquid alkanes, thereby eliminating the need for the further APD/H processing step.

In contrast to our promising results for aldol-condensation of HMF with acetone, the cross-condensation of HMF and furfural with dihydroxyacetone, glyceraldehydes and hydroxyacetone

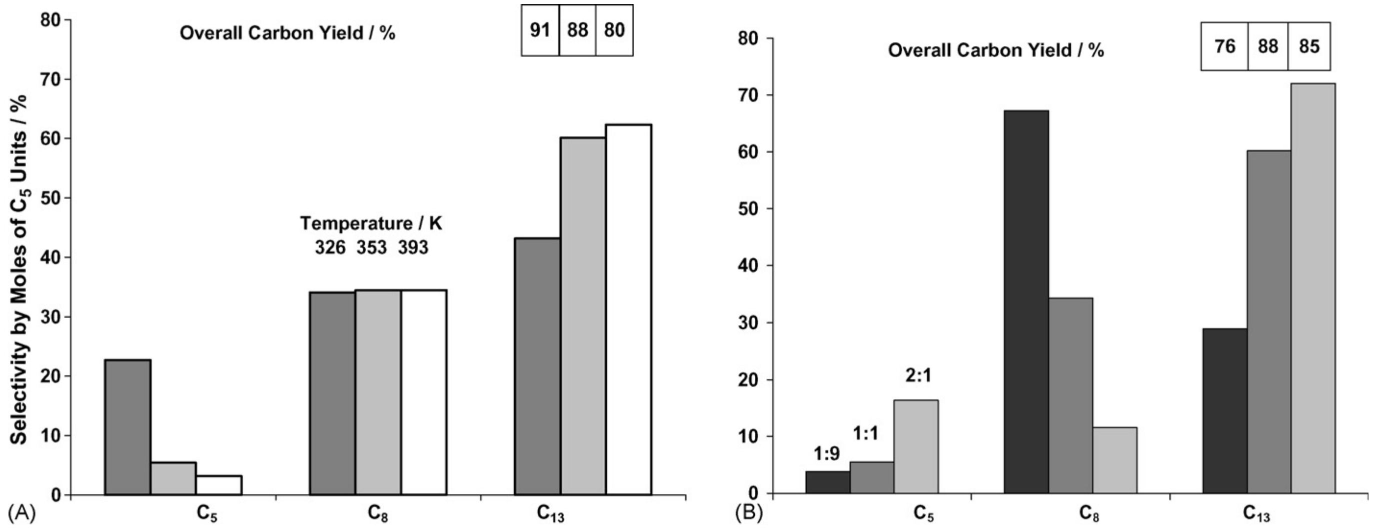

Fig. 10. Selectivity based on C_5 (furfural:acetone) units and overall carbon yields in the aqueous phase after aldol-condensation followed by hydrogenation over 5 wt% Pd/MgO–ZrO_2 catalyst. (A) Aldol-condensation of furfural with acetone (molar ratio of 1:1) over fresh catalyst at various condensation temperatures. (B) Aldol-condensation of furfural with acetone at 353 K over fresh catalyst at various molar ratios of co-reactants. (For detailed reaction conditions and figure adaptation see Ref. [41].)

resulted in less than 30% of alkanes products heavier than C_5 and C_6 reactants [7], even though a large fraction of HMF and furfural disappeared as observed by HPLC. Thus, although it is possible to cross-condense these molecules to form heavier alkanes, the selectivities for these processes will need to be improved. Similarly, selective hydrogenation of furfural to hydrogenate the furan ring showed poor selectivity (<6%) toward tetrahydrofurfural (THF2A) in the presence of water but improved results (>20%) were observed in presence of CH_2Cl_2 as solvent. However, good yields of THF2A were obtained by preferential dehydrogenation of tetrahydrofurfuryl alcohol in presence of Cu/SiO_2 catalyst to form a C_{10} precursor molecule for liquid alkanes.

7. Summary and outlook

Various challenges remain in the conversion of carbohydrate feedstocks to produce liquid alkanes by the combination of dehydration, aldol-condensation/hydrogenation, and dehydration/hydrogenation processing. Although fructose can be efficiently converted to HMF in high yields at high concentrations using a biphasic system, it is important to process glucose with similar efficiency, because glucose is the most abundantly available carbohydrate in biomass. Taking advantage of similar processing conditions for acid hydrolysis and dehydration, these two steps can be potentially combined in a single-reactor system, as demonstrated in this paper for fructose precursors, to allow the single-step conversions of other inexpensive and abundantly available polysaccharides such as hemicelluloses, starch and cellulose. In this respect, it is important to note that each sugar has different dehydration reaction characteristics in similar processing environments, and hence it is a challenge to develop a unified strategy to process a wide variety of feedstock molecules. For example, only the fructose half of sucrose is converted to HMF at 363 K in the presence of resin catalyst, leaving the glucose half of the molecule unreacted. It would be advantageous to develop new catalytic materials that can process both the fructose and glucose molecules together to form HMF effectively, thereby making efficient use of carbon in sucrose. It was seen that HMF selectivity improved in the presence of a hydrophilic polymer such as PVP that contained NMP moieties [49]. Similarly, it could be possible to graft DMSO onto a polymer backbone [50] or deposit it on a solid surface such as silica [51] to provide benefits similar to the DMSO solvent environment, thereby eliminating the energy intensive isolation procedure for HMF separation from DMSO.

As seen in Fig. 3, various carbonyl-containing species can be derived from carbohydrates or carbohydrate-derived molecules such as furfural and HMF that can be condensed to form heavier molecules. For example, levulinic acid is industrially produced in 50–70% yield from various biomass resources using H_2SO_4 [52]. It is possible that levulinic acid could be cross-condensed with HMF or furfural to form monomer and dimer species ranging from C_{10}–C_{17} that can be converted to branched alkanes upon APD/H processing. Similarly, the low selectivities of liquid alkanes we achieved from dihydroxyacetone and glyceraldehydes could be improved by the development of new base catalysts. In addition, molecules such as 2,5-furandicarboxyaldehyde and tetrahydrofuran-dicarboxyaldehyde have a carbonyl group on either side of the ring, thereby potentially providing a possibility for polymerization using acetone as a linking molecule to form much heavier products. However, it is important to control the reaction to obtain the products in the desired molecular weight range. As shown earlier, it is important to understand the structure of the products and their solubility characteristics to effectively process them to liquid alkane fuels. Another option is to separate the insoluble monomer and dimer compounds from the aqueous solution and then hydrogenating these compounds in ethanol to produce fuel additives for P-series fuel or hydrogenating these compounds in liquid alkanes to produce oxygenated diesel fuel additives.

Our results show that it is technically possible to convert carbohydrate feedstocks to produce liquid alkanes by the combination of dehydration, aldol-condensation/hydrogenation, and dehydration/hydrogenation processing; however, further optimization of these processes is required to decrease the overall number of separate steps (and reactors) required in this conversion. However, whereas the petrochemical refinery has reached its present state of efficiency by continuous improvement over the past 50 years, the biorefinery is in its infancy, and our work represents a possible direction for further research in transitioning toward a carbohydrate-based economy.

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