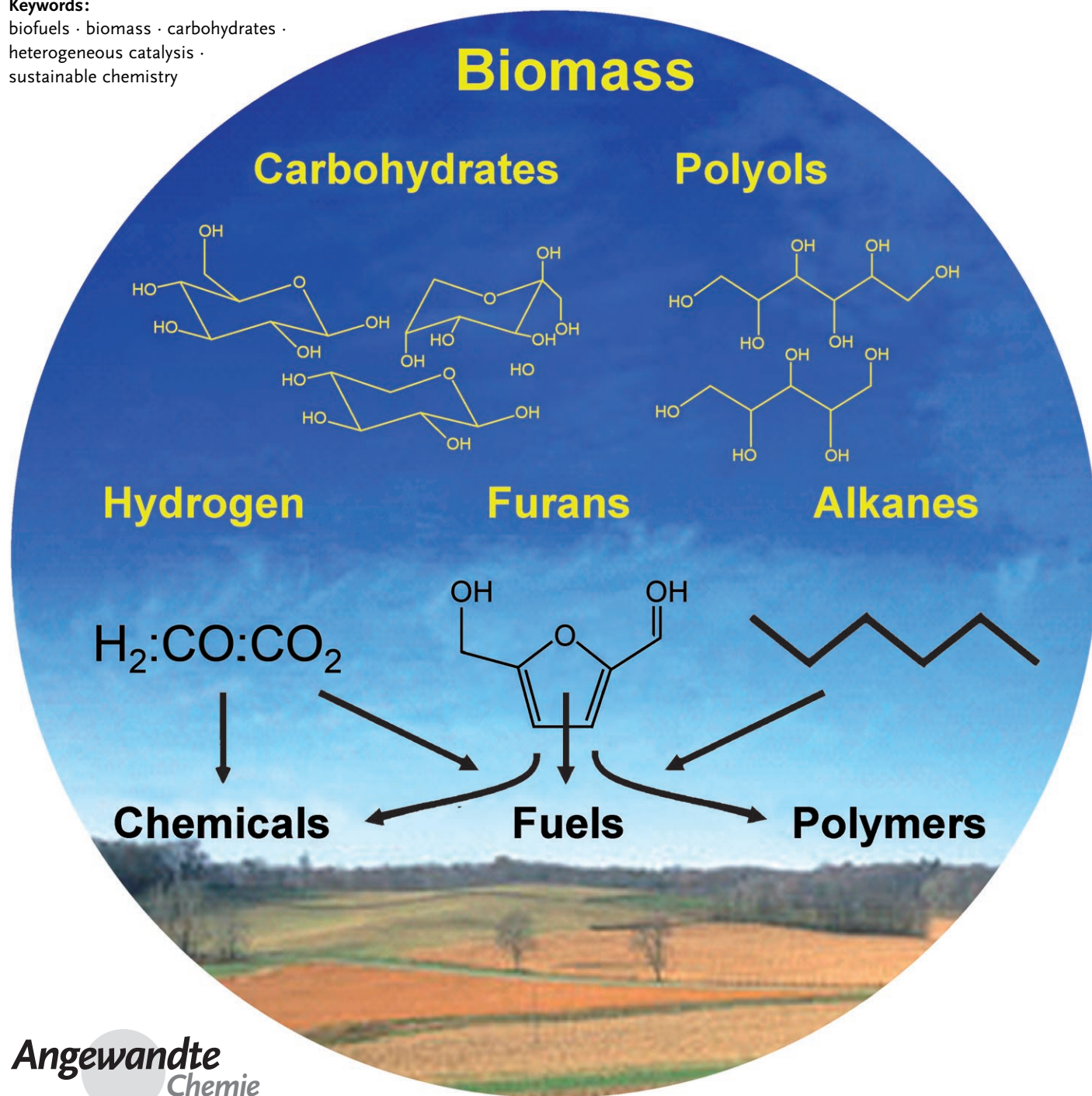


# Liquid-Phase Catalytic Processing of Biomass-Derived Oxygenated Hydrocarbons to Fuels and Chemicals

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**Keywords:**

biofuels · biomass · carbohydrates ·  
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sustainable chemistry



**B**iomass has the potential to serve as a sustainable source of energy and organic carbon for our industrialized society. The focus of this Review is to present an overview of chemical catalytic transformations of biomass-derived oxygenated feedstocks (primarily sugars and sugar-alcohols) in the liquid phase to value-added chemicals and fuels, with specific examples emphasizing the development of catalytic processes based on an understanding of the fundamental reaction chemistry. The key reactions involved in the processing of biomass are hydrolysis, dehydration, isomerization, aldol condensation, reforming, hydrogenation, and oxidation. Further, it is discussed how ideas based on fundamental chemical and catalytic concepts lead to strategies for the control of reaction pathways and process conditions to produce  $H_2/CO_2$  or  $H_2/CO$  gas mixtures by aqueous-phase reforming, to produce furan compounds by selective dehydration of carbohydrates, and to produce liquid alkanes by the combination of aldol condensation and dehydration/hydrogenation processes.

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## 1. Biomass and Biorefineries

The consumption of petroleum has surged during the 20th century, at least partially because of the rise of the automobile industry. Today, fossil fuels such as coal, oil, and natural gas provide more than three quarters of the world's energy. Unfortunately, the growing demand for fossil fuel resources comes at a time of diminishing reserves of these non-renewable resources, such that the worldwide reserves of oil are sufficient to supply energy and chemicals for only about another 40 years, causing widening concerns about rising oil prices.<sup>[1]</sup> Biomass can serve as a source for both energy and carbon, and being renewable it is the only sustainable source of energy and organic carbon for our industrial society.

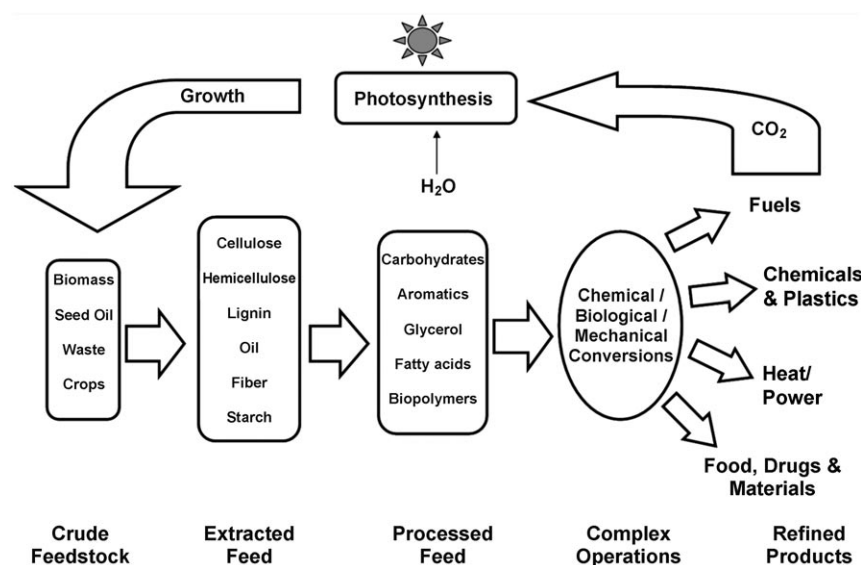
Moreover, production of energy from biomass has the potential to generate lower greenhouse gas emissions compared to the combustion of fossil fuels, because the  $CO_2$  released during energy conversion is consumed during subsequent biomass regrowth. In this respect, the "Roadmap for Biomass Technologies", a report authored by 26 leading experts, has predicted that by 2030, 20 % of transportation fuel and 25 % of chemicals will be produced from biomass.<sup>[2]</sup> To achieve these goals, a recent report from the US Department of Energy (US DOE) and the US Department of Agriculture (USDA) has estimated that the US could produce 1.3 billion dry tons of biomass per year without major changes in agricultural practices and still meet its food, feed, and export demands.<sup>[3]</sup> While corn-to-ethanol and oil-to-biodiesel have limited capacity to fulfill these goals, technology development for processing more abundant lignocellulosic biomass for fuels and materials will be critical.

The US National Renewable Energy Laboratory (NREL) has described a biorefinery as a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. Figure 1 illustrates

the conversion of biomass into bioproducts and/or energy which involves a series of interconnected feed streams, processes, and chemical intermediates. By utilizing new chemical, biological and mechanical technologies, the biorefinery provides a means of transitioning to a more energy-efficient and environmentally sustainable chemical and energy economy. In an integrated biorefinery, production of high-value chemicals will become the economic driver, supporting the production of high-volume, low-value transportation fuels and leading to profitable operations to meet energy demand. The biorefinery of the future will be analogous to the petrochemical refinery of the present: a highly integrated system of processes that are optimized for energy efficiency and resource utilization. Indeed, the success of the petrochemical industry can be attributed in part to an understanding of conversion processes and chemical mechanisms at a fundamental level. Similarly, the future success of biorefineries will require a fundamental understanding of the types of processes best suited for converting the various chemical moieties into biomass-derived constituents. Indeed, Bozell has identified *technology development* as the biggest challenge to bridge the gap between the concept and realization of a bio-based chemical industry.<sup>[4]</sup> However, whereas the petrochemical refinery has reached its present

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**Figure 1.** Overview of the processing of crude feedstocks to refined products in a sustainable biorefinery.

state of efficiency by continuous improvement over the past 50 years, the biorefinery is in its infancy.

The development of a bio-based industry requires the evaluation of a broad range of conversion technologies, including enzymatic, catalytic, and thermochemical processes. These conversion processes may take place in the gas phase or, more typically, could involve aqueous to supercritical phase conditions, spanning the range from low-temperature isomerization of carbohydrates to high-temperature gasification of biomass. In this respect, the US DOE has commissioned a study to identify the top 12 value-added chemicals that can be produced from carbohydrates and synthesis gas, and this study has discussed the technical limitations involved in the related biomass conversion processes.<sup>[5]</sup>

The focus of this Review is to present an overview of chemical catalytic transformations of carbohydrate-derived molecules in the liquid phase to value-added chemicals and fuels, with specific examples emphasizing the development of catalytic processes based on an understanding of the fundamental reaction chemistry. More generally, many options exist for the production of biofuels and products using biological processes at low temperature (300–400 K) or thermochemical processes at higher temperatures (typically

> 800 K). For example, research is being conducted to develop new and improved enzymes that transform sugars to ethanol for biofuels. Similarly, oils can be converted for biodiesel production and lignin can be transformed to valuable aromatic compounds or combusted to meet the energy requirements of a biorefinery. In this Review, we discuss selective conversions of biomass-derived oxygenated feedstocks (sugars and sugar-alcohols) with chemical catalysts at low temperatures (typically lower than 600 K) and in the liquid phase. Through the examples outlined in this Review we hope to 1) illustrate opportunities for the synthesis of novel catalytic materials tailored for the selective processing of carbohydrate structures, 2) demonstrate the important role that the solvent plays in the processing of different carbohydrates, and 3) demonstrate how an understanding of fundamental reaction chemistry for different types of reactions (e.g., dehydration, aldol condensation, hydrogenation) can lead to new approaches for specific processes.

## 2. Processing of Petroleum and Biomass

Petroleum feeds usually have a low extent of functionality (e.g.,  $-\text{OH}$ ,  $-\text{C}=\text{O}$ ,  $-\text{COOH}$ ) which makes these feeds directly suitable for use as fuels after appropriate catalytic processing (e.g., cracking to control molecular weight, isomerization to control octane number). In contrast, functional groups must be added to petroleum-derived feeds to produce chemical intermediates, and the challenge in this field is to be able to add these groups selectively (e.g., to add  $-\text{C}=\text{O}$  groups without complete oxidation of the organic reactant to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ). Unlike petroleum which contains limited functionality, biomass-derived carbohydrates contain excess functionality for use as fuels and chemicals, and the challenge in this field is to develop methods to control the functionality in the final product. Consider, for example, the selective dehydration of hexoses to produce hydroxymethylfurfural (HMF). Indeed, HMF and its ensuing 2,5-disubstituted furan derivatives can replace key petroleum-based building blocks.<sup>[5]</sup> The challenge associated with the production of HMF from fructose and glucose is depicted in Scheme 1. Although

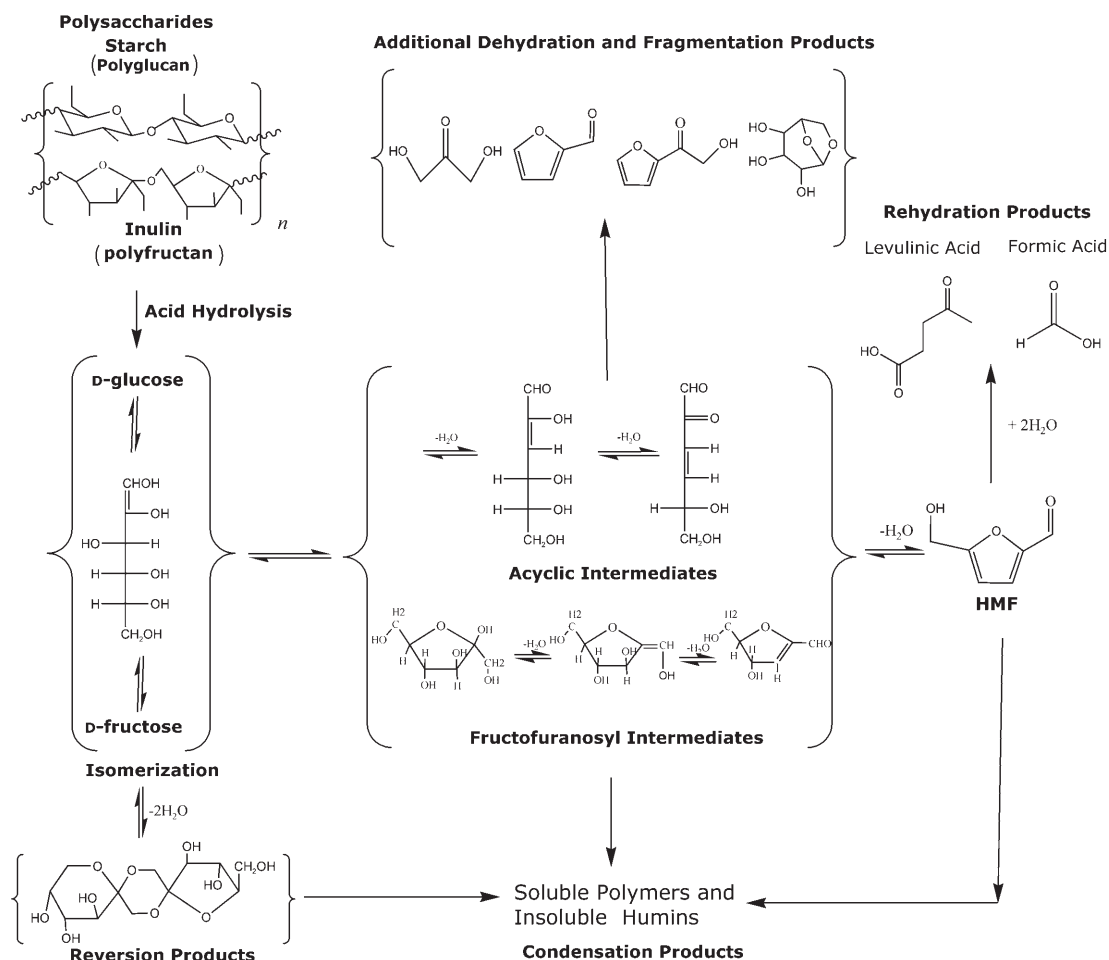


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Juben Chheda, born in Mumbai, India, earned his BS degree in chemical engineering from Mumbai University (1999) and his MS degree from Cleveland State University (2002). He then worked as a Research and Development Engineer at Aspen Technology Inc., MA. He recently completed his PhD at the University of Wisconsin–Madison (2007), working with Prof. Dumesic to develop liquid-phase catalytic technologies for the conversion of biomass-derived carbohydrates into fuels and chemicals, and is currently working at Shell Oil.





**Scheme 1.** Reaction pathways for acid-catalyzed dehydration of polysaccharides (containing hexose monomer units) to 5-hydroxymethylfurfural (HMF). Structures in brackets correspond to representative species. (Adapted from Ref. [70].)

various acid catalysts have been studied in the presence of different reaction systems such as water, organic solvents, and biphasic systems, the industrial production of HMF is currently impeded by high costs of manufacturing.<sup>[6]</sup> Similarly, as shown in Scheme 2, it is possible to produce a wide variety of potential products from a given carbohydrate reactant (e.g., glucose in this example), thus making carbohydrates a particularly flexible, but also a challenging, class of feedstock to process. Indeed, because carbohydrates comprise the main class of biomass compounds, any biomass utilization strategy

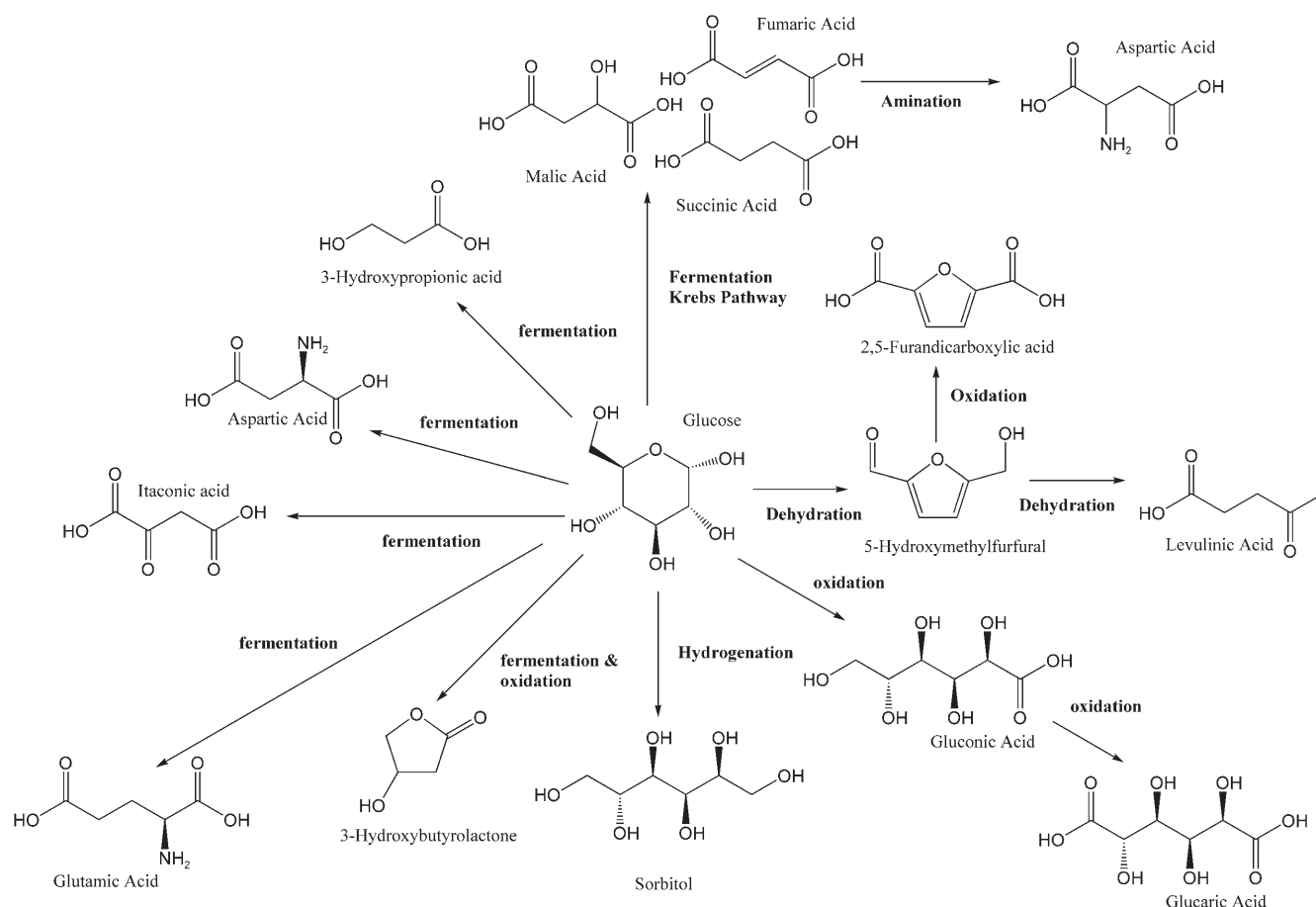
must involve the effective conversion of these compounds into bioproducts and/or energy.

Because of the high extent of functionality, carbohydrate feeds have low volatility and high reactivity and they must typically be processed by liquid-phase technologies. In addition, in view of their hydrophilic properties, liquid-phase processing of carbohydrate feeds is typically carried out in the aqueous phase or under biphasic conditions employing an aqueous and an organic phase. In general, a variety of fuels and chemical intermediates can be produced from carbohydrates by employing various types of reactions including hydrolysis, dehydration, isomerization, aldol condensation, reforming, hydrogenation, and oxidation. The heterogeneous catalysts used for these reactions can include acids, bases, metals, and metal oxides. Several types of reactions typically occur during a given process, allowing the opportunity to use multifunctional catalysts.

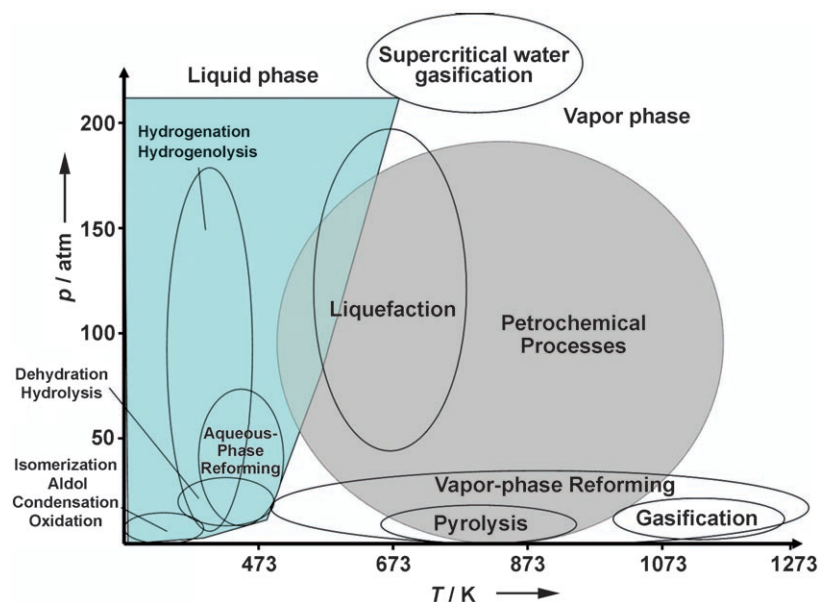
Figure 2 shows a qualitative diagram of the regimes of temperature and pressure at which petroleum and carbohydrate feedstocks are typically processed. Petroleum processes are usually conducted at elevated temperatures, and many of these processes are carried out in the vapor phase. Thermochemical processing of biomass-derived feedstocks, such as gasification, liquefaction, pyrolysis, and supercritical treat-



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**Scheme 2.** Top value-added chemicals from glucose (according to Werpy and Peterson<sup>[5]</sup>)



**Figure 2.** Diagram of approximate reaction conditions for the catalytic processing of petroleum versus biomass-derived carbohydrates.

ments, involves high-temperature treatment of biomass (these gas and supercritical processes will not be addressed in this

Review). Biomass-derived carbohydrate feeds are usually treated at mild temperatures, and most of these processes are carried out in the liquid phase. Reactions such as hydrolysis, dehydration, isomerization, oxidation, aldol condensation, and hydrogenation are often carried out at temperatures near or below 400 K. Hydrogenolysis and hydrogenation reactions are usually carried out at higher temperatures (e.g., 470 K), and aqueous-phase reforming is carried out at slightly higher temperatures (e.g., 500 K) and at higher pressures to maintain the water in the liquid state (> 50 atm). Vapor-phase reforming of oxygenated hydrocarbons can be carried out over a wide range of temperatures and at modest pressures (e.g., 10 atm).

### 3. Thermodynamic Considerations for Carbohydrate Processing Reactions

The conversion of biomass-derived oxygenates to fuels and chemicals involves the combination and/or coupling of various types of reactions, including hydrolysis, dehydration, reforming, C–C hydrogenolysis, C–O hydrogenolysis, hydrogenation, aldol condensation, isomerization, selective oxidation, and water gas shift.

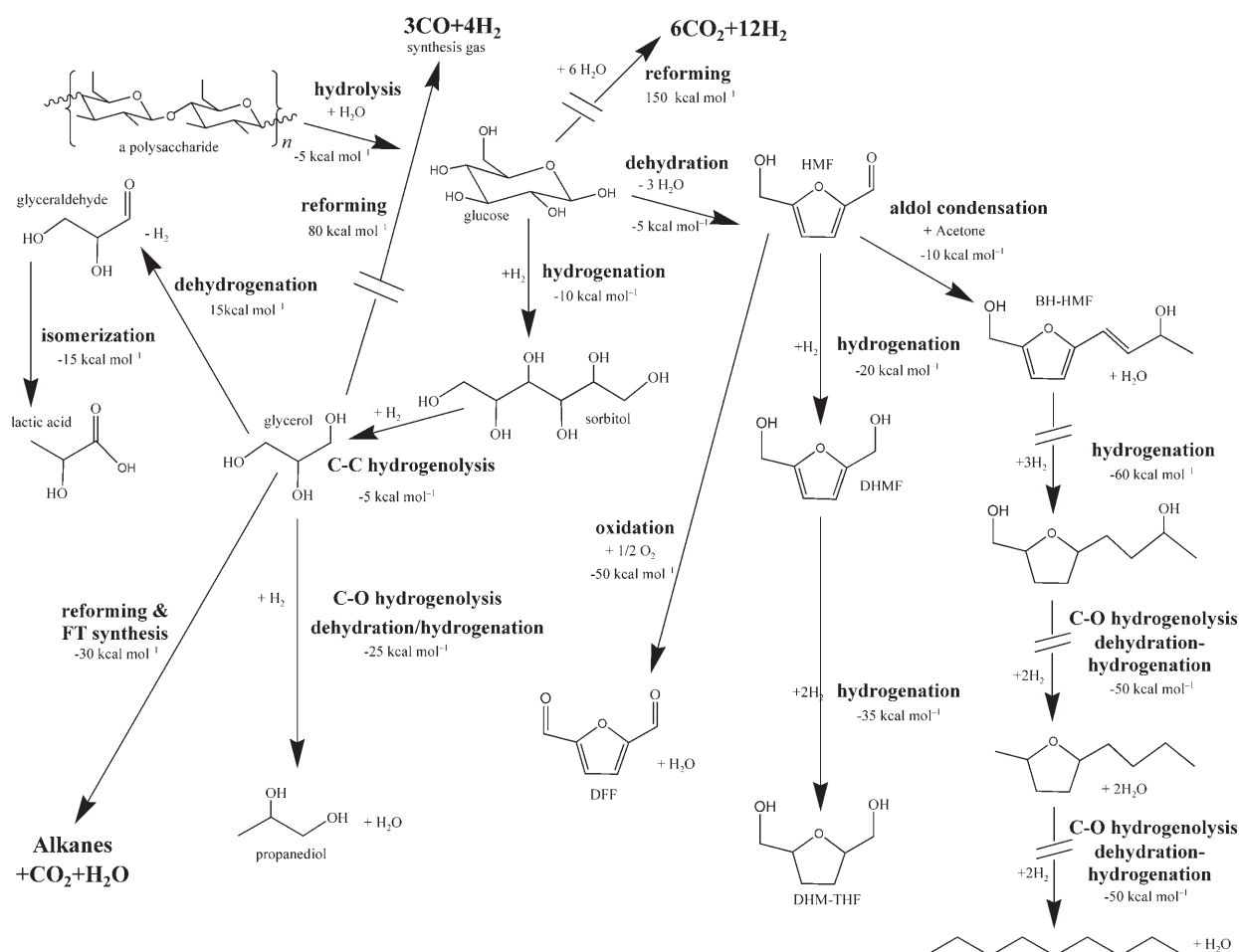
Scheme 3 presents a representation of the energy changes associated with the aforementioned reactions at 300 K and 1 atm for selected examples, where exothermic reactions (i.e., negative changes in enthalpy) are represented as moving toward the bottom of the scheme and endothermic reactions (i.e., positive changes in enthalpy) are represented as moving toward the top.

Hydrolysis of a polysaccharide to monosaccharides is nearly neutral energetically (e.g.,  $-5 \text{ kcal mol}^{-1}$  for the hydrolysis of sucrose to glucose and fructose), as is the subsequent dehydration of glucose to form HMF. In contrast to these steps where water is added or removed from biomass-derived carbohydrates, the reforming of glucose with water to form  $\text{CO}_2$  and  $\text{H}_2$  is a highly endothermic reaction ( $150 \text{ kcal mol}^{-1}$  for glucose). This formation of  $\text{CO}_2$  and  $\text{H}_2$  may be considered to be a catalytic decomposition of the sugar to form  $\text{CO}$  and  $\text{H}_2$ , combined with the conversion of  $\text{CO}$  and  $\text{H}_2\text{O}$  to produce  $\text{CO}_2$  and  $\text{H}_2$  (i.e., the water gas shift reaction,  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ , which is exothermic by  $10 \text{ kcal mol}^{-1}$ ). In this respect, half of the  $\text{H}_2$  is derived from the sugar molecule and the other half is derived from  $\text{H}_2\text{O}$ . The change in the Gibbs free energy for the overall reforming reaction is favorable at modest temperatures and above (e.g.,  $-50 \text{ kcal}$

$\text{mol}^{-1}$  for glucose at 400 K) because of the large increase in entropy for the reaction.

Hydrogenation reactions are typically exothermic. For example, the enthalpy change for the hydrogenation of glucose to sorbitol is equal to approximately  $-10 \text{ kcal mol}^{-1}$ ; the hydrogenation of HMF to 2,5-di(hydroxymethyl)furan (DHMF) has an enthalpy change of about  $-20 \text{ kcal mol}^{-1}$ ; and the enthalpy change for the hydrogenation of the furan ring in DHMF to produce 2,5-di(hydroxymethyl)tetrahydrofuran (DHM-THF) is about  $-35 \text{ kcal mol}^{-1}$  (or about  $-18 \text{ kcal per mol of H}_2$ ). For comparison, we note that the enthalpy change for hydrogenation of a  $\text{C}=\text{C}$  bond in an olefin is about  $-25$  to  $-30 \text{ kcal mol}^{-1}$ . Thus, it is thermodynamically more favorable to hydrogenate the  $\text{C}=\text{C}$  bonds in olefins, compared to hydrogenation of  $\text{C}=\text{O}$  bonds or the  $\text{C}=\text{C}$  bonds in the furan ring, and it is thermodynamically more favorable to hydrogenate these latter bonds than it is to hydrogenate a carbohydrate to its sugar-alcohol (e.g., glucose to sorbitol).

Cleavage of  $\text{C}-\text{C}$  bonds in the presence of hydrogen is termed  $\text{C}-\text{C}$  hydrogenolysis, and such reactions are nearly neutral energetically (e.g.,  $-5 \text{ kcal mol}^{-1}$  for the hydrogenolysis of sorbitol to produce two molecules of glycerol). In contrast,  $\text{C}-\text{O}$  hydrogenolysis reactions are highly exother-



**Scheme 3.** Enthalpic energy changes at 300 K and 1 atm for principal reactions involved in the conversion of carbohydrates into fuels and chemicals. Exothermic reactions are represented as moving toward the bottom of the scheme, and endothermic reactions are represented as moving toward the top.

mic. As an example, the enthalpy change for C–O hydrogenolysis of glycerol to produce propanediol and water is about  $-25 \text{ kcal mol}^{-1}$ . It is important to note that C–O hydrogenolysis can also be accomplished by a two-step process involving dehydration (catalyzed by an acid or a base) followed by hydrogenation (catalyzed by a metal). Because dehydration reactions are energetically neutral and hydrogenation reactions are highly exothermic, the combined overall process is a highly exothermic one.

Another type of reforming reaction is the production of CO/H<sub>2</sub> gas mixtures (called synthesis gas or syngas) from biomass-derived oxygenated hydrocarbons. This route for production of synthesis gas is carried out by minimizing the extent of the water gas shift reaction, for example, by minimizing the concentration of water in the feed. As seen in Scheme 3, the formation of synthesis gas from glycerol is highly endothermic, with an enthalpy change of about  $80 \text{ kcal mol}^{-1}$ . This formation of synthesis gas is highly beneficial for the biorefinery, because synthesis gas can be used as a source for fuels and chemicals, for example, in Fischer–Tropsch or methanol synthesis. As an example, the conversion of synthesis gas to alkanes (along with CO<sub>2</sub> and water) is highly exothermic (e.g.,  $-110 \text{ kcal mol}^{-1}$ ), such that the overall conversion of glycerol to alkanes by the combination of reforming and Fischer–Tropsch synthesis is mildly exothermic, with an enthalpy change of about  $-30 \text{ kcal}$  per mole of glycerol.<sup>[7]</sup>

A useful synthetic reaction that can be employed to produce C–C bonds between biomass-derived molecules is the aldol condensation. For example, aldol condensation of HMF with acetone leads to a C<sub>9</sub> species (3-hydroxybutenyl)-hydroxymethylfuran (BH-HMF).<sup>[8]</sup> This step is mildly exothermic, with an enthalpy change of about  $-10 \text{ kcal mol}^{-1}$ . The subsequent hydrogenation and C–O hydrogenolysis (or dehydration-hydrogenation) steps involved in the conversion of BH-HMF to a C<sub>9</sub> alkane are highly exothermic (with enthalpy changes of about  $-20$  to  $-25 \text{ kcal}$  per mole of H<sub>2</sub>).

While the production of fuels from biomass-derived carbohydrates involves reduction reactions, the production of chemical intermediates may involve oxidation reactions, such as the conversion of alcohols into aldehydes and carboxylic acids. These oxidation reactions are highly exothermic, as illustrated in Scheme 3 with the oxidation of HMF to form diformylfuran (DFF; enthalpy change of  $-50 \text{ kcal mol}^{-1}$ ).

Another class of important reactions for biomass conversion involves isomerization processes. For example, the conversion of glucose into fructose is of importance for the production of HMF, because higher rates and selectivities for dehydration of fructose to HMF are achieved compared to the case for glucose. The conversion between these two sugars is nearly neutral energetically. In contrast, the isomerization of a hydroxyaldehyde (i.e., a sugar) to a carboxylic acid is highly exothermic. As shown in Scheme 3, the dehydrogenation of glycerol to glyceraldehyde is highly endothermic with an enthalpy change of about  $15 \text{ kcal mol}^{-1}$ , and the isomerization of glyceraldehyde to lactic acid is exothermic with an enthalpy change of  $-15 \text{ kcal mol}^{-1}$ , such that the overall conversion of glycerol into lactic acid is about neutral energetically. The

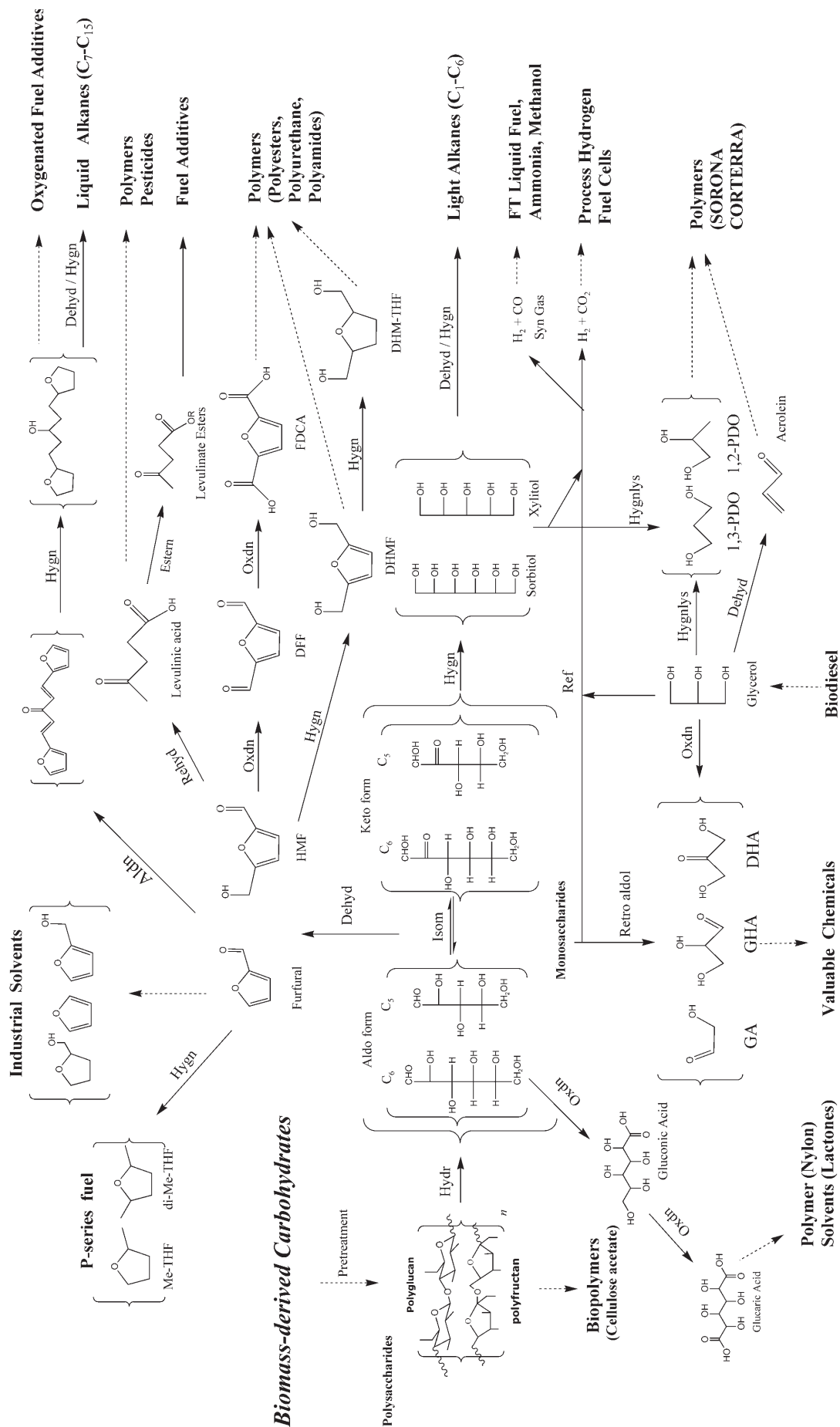
thermodynamically favorable formation of carboxylic acids from sugars (by benzilic acid rearrangement) and sugar-alcohols (by dehydrogenation and benzilic acid rearrangement) often leads to the formation of acids during processing of biomass feeds.<sup>[9]</sup>

#### 4. Reaction Classes for the Catalytic Conversion of Carbohydrate-Derived Feedstocks

A variety of chemical intermediates can be obtained using the aforementioned types of reactions (Scheme 4) starting with a polysaccharide feed. The development of processing technologies for carbohydrates requires an understanding of the fundamental chemistry and the nature of the catalyst. For example, acid hydrolysis of polysaccharides can be combined with dehydration of monosaccharides to form high-value furan compounds, such as furfural and HMF, in a single reactor system, because each of these reactions requires an acid catalyst at temperatures ranging from 370–470 K, thereby eliminating a separate hydrolysis step. Similarly, conversion of sugar alcohols, such as sorbitol, using aqueous-phase reforming can be tuned to produce H<sub>2</sub> over catalysts consisting of platinum on neutral supports or to produce light alkanes by adding an acidic functionality to the catalyst.<sup>[10,11]</sup> In this Section, we introduce examples of mono- and multi-functional catalysts as applied to various types of reactions involving biomass-derived oxygenates (primarily carbohydrates and/or carbohydrate-derived compounds) as feed molecules.

##### 4.1. Hydrolysis

Hydrolysis is one of the major processing reactions of polysaccharides in which the glycosidic bonds between the sugar units are cleaved to form simple sugars like glucose, fructose, and xylose and partially hydrolyzed dimer, trimer, and other oligomers. The challenge is to identify the reaction conditions and catalysts to convert a diverse set of polysaccharides (such as cellulose, hemicellulose, starch, inulin, and xylan) obtained from a variety of biomass sources. Hydrolysis reactions are typically carried out using acid or base catalysts at temperatures ranging from 370 to 570 K, depending on the structure and nature of the polysaccharides. Acid hydrolysis is more commonly practiced because base hydrolysis leads to more side reactions and thus lower yields.<sup>[12]</sup> Acid hydrolysis proceeds by C–O–C bond cleavage at the intermediate oxygen atom between two sugar molecules.<sup>[12]</sup> Often the reaction conditions can lead to further degradation of sugars to products such as furfural and HMF that may be undesirable. Cellulose, the most abundant polysaccharide with  $\beta$ -glycosidic linkages, is the most difficult material to hydrolyze because of its high crystallinity. Both mineral acids and enzymatic catalysts can be used for cellulose hydrolysis, with enzymatic catalysts being more selective.<sup>[13]</sup> The highest yields of glucose achieved for cellulose hydrolysis with concentrated mineral acids are typically less than 70%, whereas enzymatic hydrolysis of cellulose can produce glucose in yields close to



**Scheme 4.** Chemical steps involved in the production of fuels and chemicals from carbohydrate-based feedstocks in a biorefinery. Furfural is derived from C<sub>5</sub> sugars and HMF is derived from C<sub>6</sub> sugars. Abbreviations for reactions: Hydr = hydrolysis; Isom = isomerization; Hygn = hydrogenation; Oxdn = oxidation; Hygnlys = hydrogenolysis; Ref = reforming; Estern = esterification; Delyd = dehydration; AlAldn = aldol condensation. Abbreviations for chemical compounds: GA = glycol-aldehyde; GHA = glyceraldehyde; DHA = dihydroxyacetone; PDO = propanediol; HMF = 5-hydroxymethylfurfural; DFF = diformylfuran; FDCA = 2,5-furandicarboxylic acid; DHMF = di(hydroxymethyl)furan; Me-THF = methyl tetrahydrofuran.



100%.<sup>[14]</sup> Hemicellulose is more open to attack at intermediate positions to break down the oligomers into single sugar molecules, thereby requiring modest temperatures and dilute acid concentrations, which minimize further degradation of the simple sugars.<sup>[13]</sup> Soluble starch (a polyglucan with  $\alpha$ -glycosidic linkages obtained from corn and rice) and inulin (a polyfructan obtained from chicory) can be hydrolyzed at modest conditions (340–420 K) to form glucose and fructose, respectively.<sup>[15,16]</sup>

#### 4.2. Dehydration

Dehydration reactions of carbohydrates and carbohydrate-derived molecules comprise an important class of reactions in the field of sugar chemistry. As seen in Scheme 4, sugars can be dehydrated to form furan compounds such as furfural and HMF that can subsequently be converted into diesel fuel additives (by aldol condensation and aqueous-phase dehydration-hydrogenation),<sup>[8]</sup> industrial solvents (e.g., furan, tetrahydrofurfuryl alcohol, furfuryl alcohol),<sup>[17]</sup> various bioderived polymers (by conversion of HMF into FDCA),<sup>[5]</sup> and P-series fuel (by subsequent hydrogenolysis of furfural).<sup>[18]</sup> Furfural is industrially produced from biomass rich in pentosan (e.g., oat hulls, etc.) using the Quaker Oats technology employing mineral acid as catalyst.<sup>[19]</sup> However, HMF is not yet a high-volume chemical in view of difficulties in cost-effective production, even though many researchers have shown promising results in a wide range of potential applications.<sup>[6,20–22]</sup> Production of HMF from sugars is a problem that illustrates the selectivity challenges involved in the processing of highly functionalized carbohydrate molecules. Dehydration of hexoses has been studied in water, organic solvents, biphasic systems, ionic liquids, and near- or supercritical water, using a variety of catalysts such as mineral and organic acids, organocatalysts, salts, and solid acid catalysts such as ion-exchange resins<sup>[23]</sup> and zeolites<sup>[24]</sup> in the temperature range of 370–470 K. Although evidence exists that supports both the open-chain and the cyclic fructofuransyl intermediate pathways (Scheme 1), it is clear that the reaction intermediates and the HMF product degrade by means of various processes.<sup>[24–27]</sup> Similarly, glycerol can be dehydrated to acrolein, a polymer intermediate used in the production of polyesters such as SORONA. Ott et al. have shown promising results using sub- and supercritical water with zinc sulfate salts as catalysts to achieve yields of acrolein of up to 80%; however, corrosion induced by water and salt at these conditions necessitates the use of expensive corrosion-resistant materials for the reaction.<sup>[28]</sup>

#### 4.3. Isomerization

Isomerization of carbohydrates is typically carried out in the presence of base catalysts at mild temperatures and in different solvents. The conversion of glucose into fructose is widely practiced for production of high-fructose corn syrup. In addition, HMF selectivity from glucose can be improved by isomerization of glucose to fructose. Isomerization is gener-

ally carried out in the presence of a base catalyst such as magnesium-aluminum hydrotalcites<sup>[29]</sup> at temperatures ranging from 310 to 350 K. Carbohydrates in solution are present as open-chain (acyclic) and as ring structures such as  $\alpha$ -furanose,  $\beta$ -furanose,  $\alpha$ -pyranose, and  $\beta$ -pyranose in varying proportions.<sup>[30]</sup> The isomerization reaction involves formation of intermediate enolate species through open-chain forms to transform aldohexoses to ketohexoses. The rate of glucose isomerization is thus dictated by the fraction of the glucose molecules that are in the open-chain form, which is governed by the solvent medium and temperature. Thus, the reaction rates are higher in aprotic solvents, such as dimethyl sulfoxide (DMSO), in which the abundance of the acyclic form is about 3% for fructose as compared to in water where it is less than 0.8%. In addition, an increase in temperature to 350 K increases the amount of open-chain form, thereby increasing the rate of isomerization.<sup>[31–33]</sup>

#### 4.4. Reforming Reactions

The production of hydrogen for fuel cells, ammonia synthesis, and other industrial operations is an essential feature of future biorefineries, similar to current petroleum refineries. Pyrolysis of solid biomass followed by reforming of bio-oils and biomass gasification are known technologies for  $H_2$  production.<sup>[14]</sup> In addition, it has recently been shown that aqueous-phase reforming (APR) can be used to convert sugars and sugar alcohols with water into  $H_2$  and  $CO_2$  at temperatures near 500 K over metal catalysts.<sup>[10]</sup> Importantly, the selectivity towards  $H_2$  can be controlled by altering the nature of the catalytically active metal sites (e.g., Pt) and metal-alloy (e.g. Ni-Sn)<sup>[34]</sup> components, and by choice of catalyst support.<sup>[35]</sup> Various competing pathways are involved in the reforming process. A good catalyst should promote C–C bond cleavage and water gas shift to convert CO into  $CO_2$ , but it should not facilitate further hydrogenation reactions of CO and  $CO_2$  to form alkanes or parallel reactions by C–O bond cleavage to form alcohols and acids.<sup>[36]</sup> It has also been demonstrated that APR can be tailored to convert sorbitol into a clean stream of light alkanes ( $C_4$ – $C_6$ ) by using a bifunctional metal-acid catalyst (e.g., Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>), wherein formation of hydrogen and  $CO_2$  takes place on a metal catalyst and dehydration of sorbitol occurs on a solid acid catalyst.<sup>[11]</sup> The combination of catalytically active sites, support, solution pH, feed concentration, process conditions, and reactor design governs the selectivity of hydrogen and alkane production using aqueous-phase processing. It has recently been shown that the APR process can be used to produce  $H_2$  from actual biomass; however, low yields (1.05–1.41 mmol per gram of carbohydrates) were obtained owing to formation of coke and by-products.<sup>[37]</sup>

#### 4.5. Aldol Condensation

Aldol condensation is a C–C bond-forming reaction generally carried out to form larger molecules at mild temperatures (300–370 K) in the presence of a base or acid

catalyst. It has been shown that various carbohydrate-derived carbonyl compounds such as furfural, HMF, dihydroxyacetone, acetone, and tetrahydrofurfural can be condensed in aqueous and organic solvents to form larger molecules ( $C_7$ – $C_{15}$ ) that can subsequently be converted into components of diesel fuel.<sup>[8]</sup> Aldol condensations require at least one carbonyl compound that has an  $\alpha$ -hydrogen atom, and the reaction is generally carried out in the presence of a base catalyst. At first, the base catalyst abstracts the  $\alpha$ -hydrogen from the carbonyl compound to form an intermediate carbanion (enolate ion) species, which can then attack the carbon atom of a carbonyl group from another molecule, which may or may not have an  $\alpha$ -hydrogen atom, to form a C–C bond. The aldol adduct can further undergo dehydration to form an unsaturated aldehyde or ketone. Factors such as reaction temperature, solvent, reactant molar ratio, structure of reactant molecules, and the nature of the catalyst determine the selectivity of the process towards heavier compounds.<sup>[38]</sup>

#### 4.6. Hydrogenation

Hydrogenation reactions are carried out in the presence of a metal catalyst such as Pd, Pt, Ni, or Ru at moderate temperatures (370–420 K) and moderate pressures (10–30 bar) to saturate C=C, C=O, and C–O–C bonds. Selective hydrogenation of the C=C bonds in the furan ring of furfural leads to formation of tetrahydrofurfural (which can be converted into a diesel fuel component by self-aldol condensation)<sup>[8]</sup> or methyltetrahydrofuran (a principal component of P-series fuel).<sup>[18]</sup> On the other hand, selective hydrogenation of the C=O bond of furfural or HMF leads to furfuryl alcohol (e.g., for furanic resins, plastics)<sup>[39]</sup> or 2,5-dihydroxymethylfuran (a monomer used in the production of new polymeric material).<sup>[22]</sup> Selectivity for the hydrogenation reaction depends on factors such as solvent, partial pressure of hydrogen, and the nature of the catalyst. Production of tetrahydrofurfuryl alcohol (THFA), a solvent in various industrial applications, requires hydrogenation of all the unsaturated bonds in furfural. For example, hydrogenation of furfuryl alcohol to THFA over Pd/C is promoted in methanol solvent because of the higher concentration of dissolved hydrogen. On the other hand, during furfural hydrogenation to THFA, a Ni-based catalyst leads to formation of by-products by reaction between methanol solvent and furfural.<sup>[40]</sup> In addition, a Ru/C catalyst, inactive without solvent, is active in the presence of methanol because of stronger adsorption of aliphatic aldehydes/ketones, indicating that the solvent can influence the adsorption-desorption characteristics of furfural on the catalyst.<sup>[40]</sup> For hydrogenation of glucose to sorbitol in a trickle-bed reactor, Ru/C has been reported to be advantageous over Raney Ni because it is more selective (99.3 % yield) and does not leach into the aqueous phase.<sup>[41]</sup> Lactic acid can also be converted into propylene glycol with Ru catalysts in the liquid phase<sup>[42]</sup> or Cu catalysts in the vapor phase.<sup>[43]</sup>

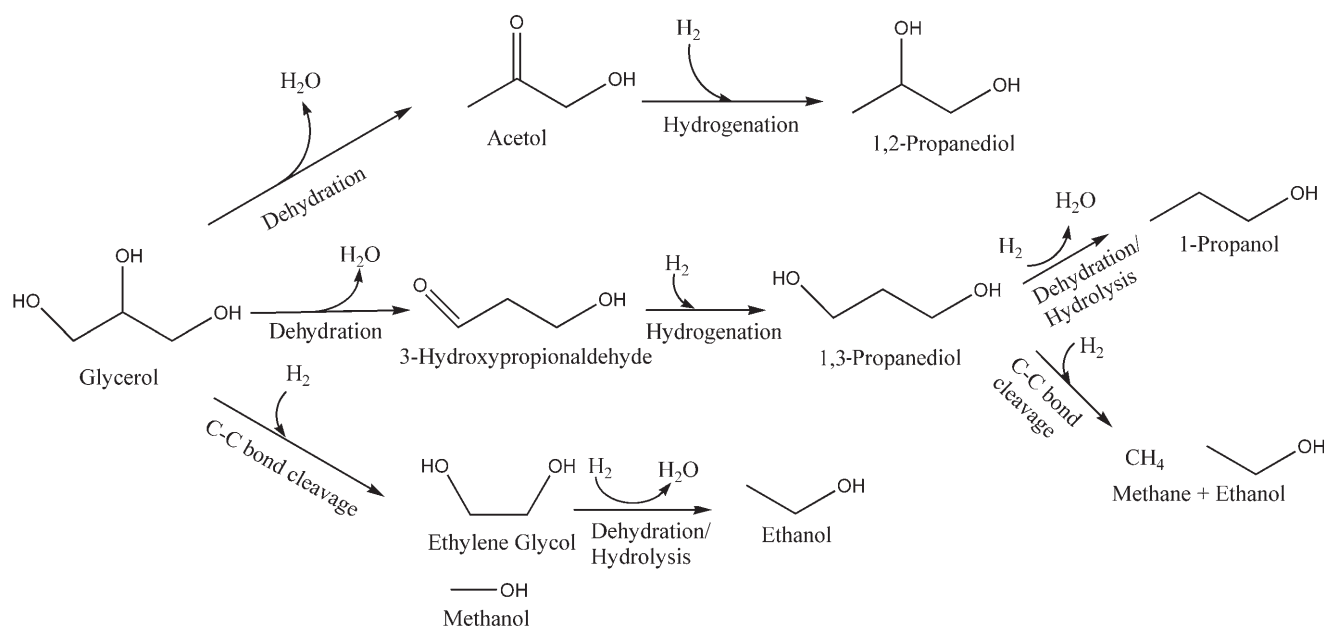
#### 4.7. Selective Oxidation

Selective oxidation is conducted to form chemical intermediates that have specific functionality, and this reaction is carried out in the presence of aqueous or organic solvents at temperatures from 330 to 420 K and oxygen pressures of 2–10 bar in the presence of supported metals (Pt, Pd, Au, Ti, Zr, V) or metal oxides and metal derivatives such as vanadyl phosphate.<sup>[44]</sup> Catalytic oxidation reactions can lead to multiple products, and thus the challenge is to direct the reaction pathways to the desired products. Selective oxidation of HMF leads to the formation of diformylfuran (DFF), which has potential applications in the synthesis of drugs, fungicides, and in preparing new polymeric materials.<sup>[45]</sup> The product distribution for this reaction depends on the type of solvent, pH, partial pressure of oxygen, temperature, and nature of the catalyst. High temperatures and almost neutral pH in the presence of a Pt/C catalyst lead to oxidation of the hydroxymethyl group to give DFF, while low temperatures and basic conditions lead to oxidation of the formyl group of HMF to form 2,5-furandicarboxylic acid (FDCA).<sup>[44]</sup> Similarly, acidic conditions in the oxidation of glycerol favor the oxidation of the secondary alcoholic group to dihydroxyacetone (DHA), while under basic conditions the primary alcoholic groups are oxidized to form glyceric acid. Addition of Bi promotes the Pt/C catalyst in the presence of base to a mechanism that involves oxidation of the secondary alcoholic group to dihydroxyacetone.<sup>[46]</sup> In a recent study of glycerol oxidation, researchers found that bimetallic catalysts (Au-Pt, Au-Pd) are more active than monometallic catalysts (Au, Pt, Pd), indicating a synergistic effect existing between Au and Pd or Pt.<sup>[46]</sup> A recent study has shown that glycerol can be converted into dihydroxyacetone (DHA) by an electrochemical route.<sup>[47]</sup>

#### 4.8. Hydrogenolysis

The hydrogenolysis of C–C and C–O bonds in polyols occurs in the presence of hydrogen (14–300 bar) at temperatures from 400 to 500 K, usually under basic conditions and with supported metal catalysts including Ru, Pd, Pt, Ni, and Cu.<sup>[48–55]</sup> The objective of hydrogenolysis is to selectively break targeted C–C and/or C–O bonds, thereby producing more valuable polyols and/or diols. These lower polyols such as ethylene glycol (EG), 1,2-propanediol (1,2-PDO), and 1,3-propanediol (1,3-PDO) have potential applications in the polymer industry.<sup>[48]</sup>

The hydrogenolysis of glycerol has received recent attention<sup>[48–52]</sup> because the cost of glycerol as a by-product is projected to decrease significantly as biodiesel production increases.<sup>[56]</sup> The hydrogenolysis pathway for glycerol over a Ru/C-amberlyst bifunctional catalyst is shown in Scheme 5.<sup>[52]</sup> Glycerol can undergo dehydration reactions to form acetol or 3-hydroxypropionaldehyde, which are then hydrogenated on the metal catalyst to 1,2- and 1,3-propanediol, respectively. It has been proposed that OH species on Ru catalyze the dehydration reaction to produce 3-hydroxypropionaldehyde, whereas the production of acetol occurs on amberlyst sites.<sup>[52]</sup>



**Scheme 5.** Reaction pathways for the conversion of glycerol into lower polyols and alcohols through hydrogenolysis.<sup>[52]</sup>

The reactivity of 1,3-propanediol is high, and it undergoes C–O or C–C bond cleavage, where C–O bond cleavage occurs through a dehydration/hydrogenation pathway. Alternatively, glycerol can undergo C–C bond cleavage to produce ethylene glycol and methanol. Copper-based catalysts have also been shown to be active for hydrogenolysis of glycerol with and without basic additives.<sup>[49–51]</sup> According to Dasari et al., the activity of supported metal catalysts for hydrogenolysis of a 80 % glycerol solution at 470 K and 15 bar decreases in the order  $\text{Ru} \approx \text{Cu} \approx \text{Ni} > \text{Pt} > \text{Pd}$ .<sup>[49]</sup>

In contrast to hydrogenolysis of glycerol, C–C bond cleavage is a desirable reaction for hydrogenolysis of large polyols (such as sorbitol). The addition of a base catalyst (e.g., NaOH) increases the rate of C–C hydrogenolysis. Wang et al. have proposed that carbon–carbon bond cleavage occurs by retro-aldol condensation, and they have studied hydrogenolysis of 1,3-diols with Raney Ni and Cu catalysts.<sup>[57]</sup> They propose that the first step in C–C bond cleavage is dehydrogenation, followed by retro-aldol condensation. The products from retro-aldol condensation are then hydrogenated. The forward aldol condensation can also occur under these conditions.

## 5. Process Developments from Chemical and Catalytic Concepts

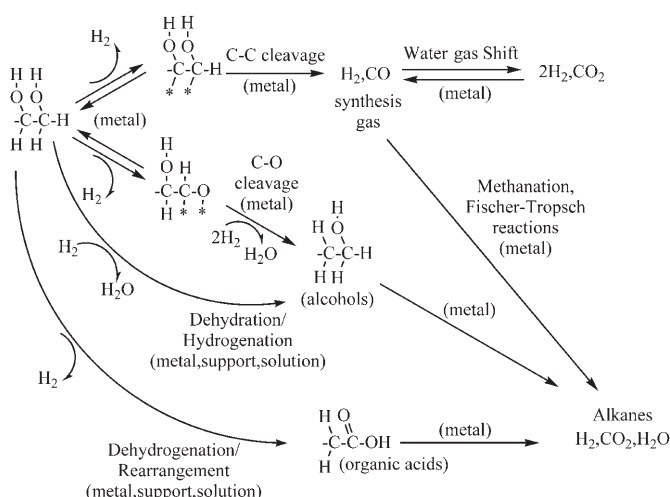
In this Section, we provide examples of using chemical and catalytic concepts to aid in the formulation of new processes for the conversion of biomass-derived carbohydrates into fuels and chemicals. For convenience, these examples are based primarily upon our own work. Overall, we hope to show that simple ideas based on fundamental chemical and catalytic concepts can lead to strategies for the control of reaction pathways and process conditions to

achieve high yields for the production of specific products from biomass-derived oxygenated hydrocarbons.

### 5.1. Conversion of Biomass into Fuels: Aqueous- versus Vapor-Phase Reforming of Oxygenated Hydrocarbons

Transportation vehicles require fuels that can be readily stored with high energy densities. Thus, while hydrogen fuel cells are capable of efficient energy conversion, the storage of sufficient amounts of hydrogen to achieve the desired transportation range is still an unsolved problem. In contrast, the conversion of oxygenated hydrocarbons into hydrogen appears to be advantageous for stationary applications, such as producing hydrogen as a reactant for chemical processes, supplying hydrogen for fuel cells (e.g., a battery charger), or producing hydrogen as a feed to an electrical generator operated using an internal combustion engine.

The essential pathways involved in the conversion of oxygenated hydrocarbons into  $\text{H}_2$  and alkanes over supported metal catalysts are depicted in Scheme 6. Metal catalysts that achieve selective cleavage of C–C bonds in oxygenated hydrocarbons that have a C/O stoichiometry of 1:1 (e.g., methanol, ethylene glycol, glycerol, xylose, glucose, sorbitol) lead first to the production of  $\text{H}_2$  and CO, with the CO being adsorbed strongly on the surface of a metal such as Pt. In the presence of water, the adsorbed CO can be converted further by the water gas shift reaction to produce  $\text{CO}_2$  and  $\text{H}_2$ . Indeed, in the presence of liquid water at temperatures near 500 K (and total pressures near 30 atm), the water gas shift equilibrium is favorable for the production of  $\text{H}_2$  and  $\text{CO}_2$ , such that the effluent gas typically contains low levels of CO, for example, about 100 ppm in the  $\text{H}_2/\text{CO}_2$  gas mixture after condensation of water vapor.<sup>[58]</sup> Thus, the combination of C–C bond cleavage and water gas shift leads to the production of



**Scheme 6.** Reaction pathways involved in the conversion of oxygenated hydrocarbons (e.g., carbohydrates) into  $H_2$  and alkanes over supported metal catalysts. (Adapted from Ref. [10].)

$H_2$ -rich gas mixtures that are appropriate for fuel cell applications as well as for chemical process applications. While the C/O stoichiometry of 1:1 is needed to obtain high selectivity towards  $H_2$ , it is important to address the importance of the source of carbohydrate feedstock.<sup>[59]</sup> While some components in biomass feeds could inhibit the APR process (such as organic acids), the primary effect of water-soluble organic compounds obtained from woody biomass that do not have a C/O stoichiometry of 1:1 would be to lead to the formation of additional amounts of alkanes (because only those carbon atoms in the molecule that are bonded to oxygen lead to the eventual formation of  $H_2$  and  $CO_2$ ).

One route for the conversion of oxygenated hydrocarbons into alkanes is achieved by following the same path shown in Scheme 6 as for the production of  $H_2/CO_2$  gas mixtures, but by suppressing the water gas shift reaction. This situation corresponds to the conversion of oxygenated hydrocarbons to  $CO/H_2$  mixtures (synthesis gas). Indeed, once the oxygenated hydrocarbon reactant has been converted into synthesis gas, it is then possible to carry out the subsequent conversion of synthesis gas into a variety of liquid products by well-established catalytic processes, such as the production of long-chain alkanes by Fischer–Tropsch synthesis and the production of methanol by methanol synthesis. The most direct way to suppress the water gas shift reaction is to operate the system in the vapor phase, such that low partial pressures of water can be achieved, in contrast to aqueous-phase operation where the partial pressure of water is controlled by vapor–liquid equilibrium. Clearly, by decreasing the partial pressure of water it is possible to alter the water gas shift equilibrium toward CO. Another means of decreasing the rate of water gas shift is to operate at higher concentrations of the oxygenated hydrocarbon reactant in water, thereby decreasing the concentration of the water reactant for the water gas shift reaction. Importantly, it is also possible to suppress the water gas shift reaction by using catalyst supports that do not activate water. In particular, it has been shown

that various oxide supports (e.g., alumina, ceria, titania) facilitate the water gas shift reaction for supported metal catalysts,<sup>[60,61]</sup> and the mechanism for this promotion is probably related to the ability of these supports to dissociate water. In contrast, this promotional effect on water gas shift is not expected to be significant for a catalyst support such as carbon. In this respect, we have shown that whereas water gas shift is significant during the conversion of glycerol and water at 620 K over a catalyst consisting of Pt supported on ceria-zirconia, the rate of water gas shift is negligible at these conditions over Pt supported on carbon.<sup>[7]</sup>

The production of synthesis gas from oxygenated hydrocarbons over a supported metal catalyst such as Pt/C may be limited at low temperatures (e.g., below 570 K) by the desorption of CO from the metal surface. In particular, the heat of CO adsorption on Pt is high (e.g., 130–180 kJ mol<sup>−1</sup>, depending on the CO coverage), and unless the CO is converted into  $CO_2$  by the water gas shift reaction, its pressure in the reactor accumulates, leading to high coverages of CO on the Pt surface. At these high CO coverages, the probability of finding adjacent Pt sites available to activate the oxygenated hydrocarbon reactant is low, leading to low rates of reaction. Thus, to produce an active catalyst for the production of synthesis gas from oxygenated hydrocarbons at low temperatures, it is necessary not only to suppress the water gas shift reaction but also to weaken the bonding of CO to the metal surface. Importantly, a decrease in the binding energy of CO to the metal surface can be achieved by using the appropriate metal alloys. For example, it has been predicted that a surface overlayer of Pt on Ru (or Re) is more stable than the diffusion of Pt into the bulk of Ru (or Re), and the strength of CO bonding to Pt on Ru (or Re) is weaker compared to the bonding of CO on a surface of Pt metal.<sup>[62]</sup> Indeed, we have found that PtRu and PtRe alloys supported on carbon are excellent catalysts for the conversion of glycerol in water into synthesis gas at temperatures below 570 K, at which temperatures Pt/C catalysts exhibit low catalytic activity.<sup>[7]</sup>

Another pathway outlined in Scheme 6 involves the formation of organic acids by dehydrogenation followed by rearrangement reactions. As noted in Section 3, a hydroxy-aldehyde is less stable than a carboxylic acid (e.g., glycer-aldehyde is less stable than lactic acid). Thus, the formation of small amounts of organic acids typically takes place during aqueous-phase processing of highly oxygenated hydrocarbons.

At this point, it is instructive to compare and contrast aqueous-phase versus vapor-phase reforming of oxygenated hydrocarbons. The production of  $H_2$  and  $CO_2$  from carbohydrate feeds requires aqueous-phase reforming (APR) conditions because of the low volatility of carbohydrates. The advantage of the APR process is that it can be used to produce  $H_2$  and  $CO_2$  from oxygenated hydrocarbons, such as glucose, that have low vapor pressures at the temperatures that can be achieved without leading to excessive decomposition of the feed. However, the need to maintain water in the liquid state requires that the APR process be operated at pressures that are higher than the vapor of water (e.g., 50 bar at 540 K). Thus, the practical range of temperatures that can



be employed is limited by the pressures that can be tolerated safely in the reactor system. While the need to operate at elevated pressures can be a disadvantage for system design, it is an advantage for the subsequent separation of  $H_2$  from  $CO_2$ . In particular, because the  $H_2/CO_2$  gas mixture is produced at elevated pressure, the  $H_2$  and  $CO_2$  can be readily separated using a membrane or by pressure-swing adsorption. Another advantage of the APR process is that nonvolatile modifiers can be added to the liquid feed to control the performance of the catalytic process (e.g., addition of basic or acidic components to adjust the pH of the aqueous carbohydrate feed stream). A possible disadvantage of the APR process is that leaching of catalyst components into the aqueous phase can take place under the reaction conditions, and the choice of catalyst support materials is limited to those that exhibit long-term hydrothermal stability (e.g., carbon, titania, zirconia).

As noted above, an important feature of APR is that these reaction conditions favor the water gas shift reaction. Furthermore, the activation energy barrier for water dissociation on surfaces of the metal catalyst appears to be lower in the liquid phase compared to the vapor phase, and the equilibrium conversion of CO and  $H_2O$  to produce  $CO_2$  and  $H_2$  is increased at the high partial pressures of water employed during the APR process. Thus, the APR process typically generates  $H_2/CO_2$  gas mixtures containing low levels of CO ( $\approx 100$  ppm). These attributes of the APR process are desirable for producing  $H_2$  containing low levels of CO, but they are a disadvantage if the goal is to produce  $H_2/CO$  gas mixtures (synthesis gas), for example, for the Fischer–Tropsch synthesis.

In contrast to the APR process, vapor-phase reforming of oxygenated hydrocarbons is best practiced on volatile reactants, such as methanol, ethylene glycol, and glycerol. Because the water is converted into steam, it is not necessary to operate at high pressures and it is possible to carry out vapor-phase reforming at elevated temperatures (e.g., 700 K) to achieve high rates of reaction. Another advantage of vapor-phase reforming conditions is that potential leaching of catalyst components need not be considered, although catalyst stability at elevated temperatures is required. Importantly, it is possible to control the extent of the water gas shift reaction under vapor-phase reforming conditions to generate  $H_2/CO/CO_2$  gas mixtures with specific  $H_2/CO$  ratios. For example, it is possible to generate  $H_2/CO_2$  gas mixtures containing small amounts of CO (e.g., 1 %) by incorporating into the catalyst specific compounds that promote the rate of water gas shift (e.g., ceria, copper). On the other hand, it is possible to produce  $H_2/CO$  gas mixtures that can be used for synthesis gas utilization steps by using catalysts over which the rate of water gas shift is slow (metals supported on carbon). Indeed, one promising application of vapor-phase reforming of oxygenated hydrocarbons is coupling of the reforming process (to produce  $H_2/CO$ ) with Fischer–Tropsch synthesis (to utilize  $H_2/CO$ ), thereby leading to conversion of the oxygenated hydrocarbon feed into liquid alkanes.

## 5.2. Conversion of Sugars into 5-Hydroxymethylfurfural (HMF)

Furan derivatives, such as furfural and HMF, can be produced from renewable biomass resources by acid-catalyzed dehydration of pentoses and hexoses, respectively. Selective dehydration of hexoses leads to formation of HMF, a polyfunctional chemical intermediate that has the potential to be a substitute for petroleum-based building blocks for various types of polymers (e.g., polyamides, polyesters).<sup>[20,22]</sup> The formation of HMF occurs by the loss of three water molecules in an acid-catalyzed dehydration of fructose or glucose. However, HMF production is generally more selective from ketohexoses (fructose) as compared to aldohexoses (glucose).<sup>[6]</sup> Scheme 1 depicts generalized reaction pathways for the production of HMF from hexoses. Isomerization, dehydration, fragmentation, reversion, and condensation processes constitute the primary reactions during decomposition of sugars.<sup>[6]</sup> The HMF product can also undergo further rehydration to form levulinic acid and formic acid in the presence of water.<sup>[63]</sup> Previous studies suggested that HMF formation can take place through an open-chain 1,2-enediol mechanism or through fructofuranosyl intermediates.<sup>[24,27,64]</sup> However, Antal et al. showed that the formation of HMF from fructose proceeds via cyclic intermediates, providing evidence such as 1) facile conversion of 2,5-anhydro-D-mannose (an intermediate enol in cyclic mechanism) to HMF; 2) facile formation of HMF from the fructose part of sucrose; and 3) lack of carbon–deuterium bond formation in HMF owing to keto–enol tautomerism in the open-chain mechanism when the reaction is carried out in  $D_2O$ .<sup>[25,26,65]</sup> Similarly, results from theoretical calculations reinforce the conclusion that cyclic reaction pathways are dominant for HMF formation from glucose and xylose.<sup>[27]</sup> While selectivity in the presence of water is low, high yields (> 90 %) can be achieved in aprotic solvents such as DMSO.<sup>[66]</sup> Previous studies suggest that fructose is predominantly present in the furanose form in aprotic solvents such as DMSO and at higher temperatures, when compared to the dominant  $\beta$ -pyranose form in pure water.<sup>[31–33]</sup> Thus, the increased percentage of furanose form in DMSO at higher temperature favorably shifts the equilibrium towards HMF formation. The abundance of  $\beta$ -fructofuranose in DMSO can be attributed to increased stability of this form as a result of intramolecular hydrogen bonding between two pairs of primary and secondary hydroxy groups. In addition, HMF degradation to levulinic acid is also prevented at low concentrations of water. Another way that HMF can degrade is by reaction with fructose or reaction intermediates through condensation processes, thereby leading to a decrease in the HMF yield. One way to counter this degradation pathway is to separate HMF from the reaction medium as it forms, as demonstrated by various researchers upon adding an organic extracting solvent.<sup>[23,24]</sup> However, poor HMF partitioning in the organic solvents leads to large amounts of solvent, thereby incurring large energy expenditure to purify the diluted HMF product.

Recently, we developed a cost-effective method to produce HMF using a biphasic batch reactor system, processing D-fructose to HMF in high yields (> 80 %) at high fructose concentrations (10–50 wt %) and delivering the

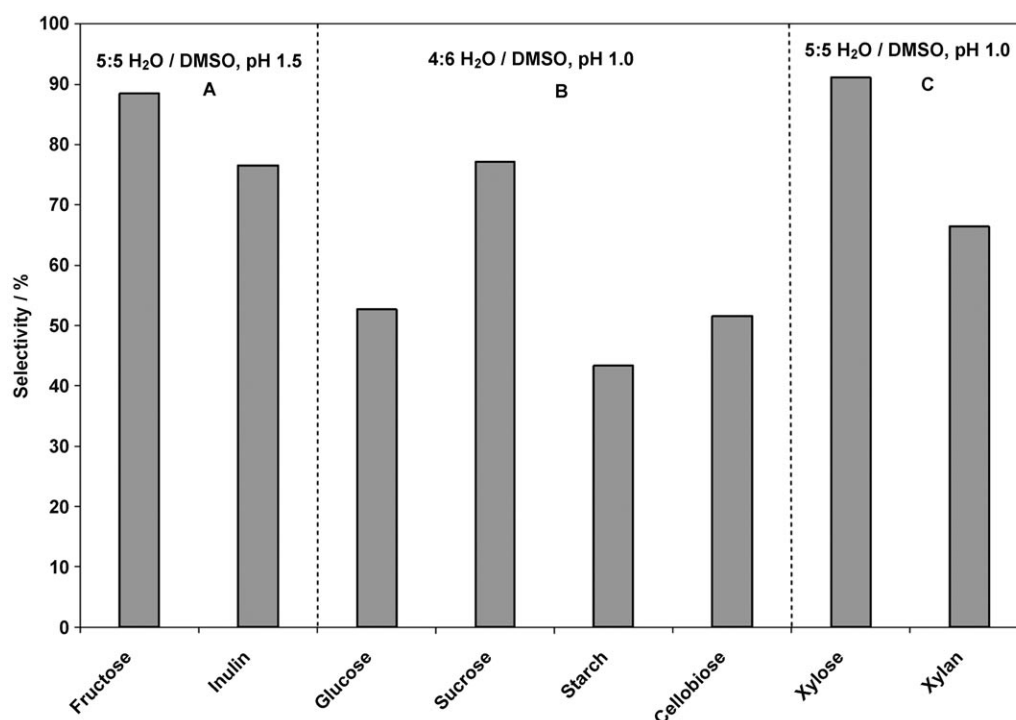
product in a separation-friendly solvent.<sup>[67]</sup> In a two-phase reactor system, the fructose is dehydrated in the reactive aqueous phase in the presence of HCl as acid catalyst with DMSO and/or poly(1-vinyl-2-pyrrolidinone) (PVP) added as modifiers to suppress the formation of by-products. The HMF product is continuously extracted into an organic phase (methylisobutylketone, MIBK) modified with 2-butanol to enhance partitioning from the reactive aqueous solution. Previous work has shown that high yields of HMF from fructose can be obtained in high-boiling solvents such as pure DMSO; however, the HMF product thermally degrades upon purification from DMSO, leading to energy-intensive separation procedures.<sup>[68]</sup> Importantly, by adding small amounts of aqueous-phase modifiers (such as DMSO and PVP) in the biphasic reactor system, the selectivity can be improved from 60 to 75%. The effectiveness of the process was further improved by optimizing the partitioning of HMF product into the organic phase, both to minimize degradation of HMF in the aqueous phase and to achieve efficient recovery in the product isolation step. The extracting power of the solvent (defined as the concentration of HMF in the organic phase divided by the concentration of HMF in the aqueous phase) decreases in the presence of aqueous-phase modifiers. In this respect, addition of 2-butanol to the organic phase helps to improve partitioning by increasing the HMF solubility in the organic phase compared to MIBK. Use of all three modifiers (DMSO, PVP, and 2-butanol) at 30 wt% fructose concentration afforded 83% selectivity for HMF at 82% conversion.<sup>[67]</sup> Increasing the concentration from 30 to 50 wt% decreased the HMF selectivity owing to higher rates of condensation reactions, but doubling the amount of the extracting solvent (7:3 MIBK/2-butanol mixture) increased the selectivity substantially. Experiments conducted at low fructose conversions in pure water and in the presence of 20 wt% DMSO indicated that DMSO enhances the rate of fructose conversion and decreases the rates of undesired parallel reactions. Alternatively, use of 1-methyl-2-pyrrolidinone (NMP) as a substitute for DMSO produced equally good selectivities but had higher carryover of NMP into the organic extracting solvent ( $\approx 5$  wt%) as compared to DMSO ( $\approx 0.8$  wt%), thereby complicating the subsequent recovery of HMF. Notably, use of PVP, a stable hydrophilic polymer that has NMP moieties along the polyethylene chain, as an aqueous-phase modifier shows the same selectivity benefit produced from NMP, but it eliminates the contamination of the organic phase owing to negligible solubility of PVP in the organic phase.

Previous work by various researchers has focused on fructose dehydration to HMF, because fructose dehydration has higher reaction rates and better selectivity to HMF as compared to when glucose is used as a feed molecule. The low yields of HMF from glucose can be attributed to stable ring structures, thereby leading to a lower fraction of open-chain forms in solution and consequently lower rates of enolization that determine the rate of HMF formation.<sup>[6]</sup> In addition, glucose forms oligosaccharides which contain reactive hydroxy groups, leading to higher rates of cross-polymerizations with reactive intermediates and HMF.<sup>[6]</sup> However, a strong incentive exists for the development of processes that utilize

cheap and abundantly available glucose directly, without requiring an additional step of glucose isomerization to fructose. In pure water, glucose dehydration to HMF is nonselective (about 6%),<sup>[69]</sup> and importantly the yields of HMF in aprotic polar solvents such as DMSO are low ( $\approx 42\%$ ) even for a 3 wt% glucose solution.<sup>[66]</sup> In this respect, the yield to HMF using the above-mentioned biphasic reactor system to process 10 wt% glucose feed solution can be improved by increasing the DMSO content to 60 wt% in the aqueous phase and using a 7:3 (w/w) mixture of MIBK/2-butanol as the extracting solvent. Specifically, the HMF selectivity increases from 11% in pure water to 53% in the presence of DMSO and the extracting solvent.<sup>[70]</sup>

Although various combinations of solvents and catalysts exist to produce HMF and furfural from one of multiple feedstocks, a single system capable of efficiently processing glucose, fructose, and xylose into HMF and furfural is still lacking. Accordingly, we studied the performance of the biphasic reactor system for the dehydration of glucose, fructose, and xylose to produce HMF and furfural, respectively, by varying the pH and DMSO content.<sup>[70]</sup> Fructose gave the highest rates and a selectivity of 89% at 50 wt% DMSO concentration and pH 1.5, while glucose displayed a selectivity of 53% in the presence of 60 wt% DMSO at pH 1.0. Similarly, the selectivity for xylose dehydration to furfural increased significantly to 91% at 50 wt% DMSO level but at pH 1.0. The dehydration process was subsequently employed to achieve the dehydration of various polysaccharide compounds at conditions optimized for their monomer units. As seen in Figure 3, dehydration of inulin, a fructose precursor obtained from chicory, gave a selectivity of 77% at high conversions, consistent with the results obtained from fructose, assuming that some losses occur during the hydrolysis of the polyfructan to fructose. Similarly, reacting sucrose, a disaccharide found in sugarcane or sugar beet which has a unit each of fructose and glucose, led to 77% selectivity at 65% sucrose conversion. If it is considered that at these processing conditions fructose would be completely converted and assuming a glucose conversion of 30%, the selectivity follows the trends set by its monomer unit (i.e. fructose (89%) and glucose (53%)). Similarly, the conversion of cellobiose (a glucose dimer with  $\beta$ -1,4-glycosidic linkages obtained from partial hydrolysis of cellulose) and soluble starch (a polyglucan containing  $\alpha$ -1,4-glycosidic linkages obtained from corn and rice) shows similar selectivity for HMF as that of its monomer glucose unit. The conversion of soluble starch gives a slightly lower value, suggesting that some loss of selectivity occurs during hydrolysis of the multiple glycosidic linkages in this polymer. Xylan (obtained from oat hulls) is a xylose polymer representative of hemicellulose, and the dehydration of this compound reveals a furfural selectivity of 66% at high conversions.

Although fructose dehydration can be conducted with 20% DMSO to achieve 75% selectivity, the glucose and fructose components of the sucrose molecule are both effectively converted into HMF by increasing the pH value to 1.0 and the DMSO content to 60%. In addition, this reaction system effectively processes polysaccharides such as starch or xylan, which have limited solubility in the aqueous



**Figure 3.** Selectivities for HMF and furfural in the dehydration of mono- and polysaccharides in water-DMSO mixtures using HCl as catalyst and MIBK/2-butanol (7:3 w/w) as an extracting solvent at 443 K. A) HMF selectivity from fructose and inulin dehydration in water/DMSO mixture (5:5 w/w) at pH 1.5. B) HMF selectivity from glucose, sucrose, starch, and cellobiose dehydration in water/DMSO mixture (4:6 w/w) at pH 1.0. C) Furfural selectivity from xylose and xylan dehydration in water/DMSO mixture (5:5 w/w) at pH 1.0. (Adapted from Ref. [70].)

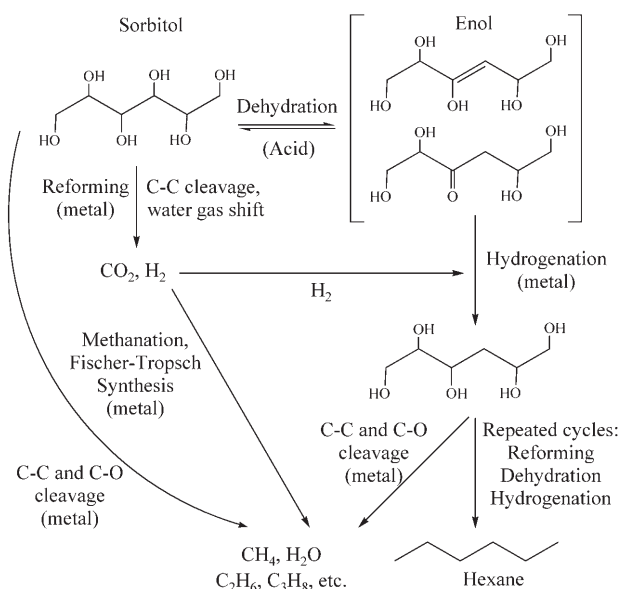
phase. Even though all sugars have the same stoichiometry, they have different structures and they exhibit widely different chemical reactivities in a similar processing environment. The results demonstrate the capability to fine-tune the biphasic reactor system to process diverse biomass-derived feedstock molecules to valuable furanic compounds by selective dehydration. By processing these highly functionalized polysaccharides, which are inexpensive and abundantly available, the need to obtain simple carbohydrate molecules by acid hydrolysis as a separate processing step is eliminated.

While the above results show that various polysaccharides can be processed using mineral acid catalysts, it is desirable to carry out dehydration using solid acid catalysts that can be easily separated from the product and recycled. In this respect, results using acidic ion-exchange catalysts at low temperature (363 K) showed lower selectivity for HMF in the presence of modifiers; however, promising results (e.g., 73 % HMF selectivity) were obtained using niobium phosphate at higher temperatures (453 K).<sup>[67]</sup> It is anticipated that these results can be further improved by synthesizing new catalytic materials such as nanoporous MCM-based materials which contain sulfonic acid groups that promote dehydration of xylose to furfural at elevated temperatures.<sup>[71]</sup> Also, while various polysaccharides can be processed with the biphasic reactor approach using higher levels of DMSO, separation of HMF from DMSO in the organic phase still remains an issue. However, as demonstrated by the effect of PVP, we anticipate that DMSO can be grafted onto a hydrophilic polymer backbone or onto a catalyst surface to provide an environment conducive for selective dehydration of various sugars to

furan compounds.<sup>[72,73]</sup> In this respect, two interesting articles have recently appeared reporting novel methods to synthesize HMF.<sup>[77,78]</sup> While the dehydration process described here shows technical feasibility, opportunities exist to improve it further by better understanding of structural rearrangements of carbohydrates in solutions and development of new catalytic materials.

### 5.3. Conversion of Biomass-Derived Carbohydrates into Liquid Alkanes

Although research involved in the storage and use of hydrogen as a clean fuel progresses, liquid alkane fuels reveal a high energy density, they are readily stored, and they are converted efficiently using internal combustion engines. In addition, the lighter alkanes can potentially be used as fuel for homogeneous charge-compression ignition (HCCI) engines that are still at the research stage. Also, it is possible to convert hexane into a mixture of C<sub>2</sub> and C<sub>10</sub> hydrocarbons by metathesis reactions,<sup>[74]</sup> such that the C<sub>2</sub> fraction can be used for polymer applications and the C<sub>10</sub> fraction can be used for blending with transportation fuels. In this respect, one of the strategies for converting oxygenated hydrocarbons into lighter alkanes (C<sub>3</sub>–C<sub>6</sub>) is to suppress the initial cleavage of C–C bonds that leads to the production of H<sub>2</sub>/CO and subsequently H<sub>2</sub>/CO<sub>2</sub> gas mixtures, and instead facilitate the cleavage of C–O bonds in the oxygenated hydrocarbon reactant. This conversion of oxygenated hydrocarbons into alkanes involves the removal of hydroxy groups by C–O



**Scheme 7.** Reaction pathways for the production of lighter alkanes from sorbitol over bifunctional catalysts containing metal and acid components. (Adapted from Ref. [11].)

hydrogenolysis or dehydration-hydrogenation processes (Scheme 7). The hydrogen required for these steps can be provided in situ by a controlled amount of aqueous-phase reforming to produce  $\text{H}_2/\text{CO}_2$  or it can be supplied from an external source. While metals such as Pt and Pd are selective for cleavage of C–C bonds in oxygenated hydrocarbons, metals such as Ni and Ru are active for cleavage of the C–O bond, leading to higher levels of alkanes in the product gas mixture. Importantly, it is possible to cleave C–O bonds in oxygenated hydrocarbons by a two-step process termed dehydration-hydrogenation (Scheme 7). In particular, an acidic support, such as silica-alumina or a zeolite, is employed to catalyze dehydration reactions, leading first to the production of olefins, ketones, and/or aldehydes (i.e., enol species), followed by the migration of these unsaturated species to metal sites on the catalyst where hydrogen is added. When this dehydration-hydrogenation strategy is employed over a catalyst consisting of Pt supported on silica-alumina and the process conditions are chosen to minimize the rate of C–C bond cleavage on Pt (i.e., operating at temperatures near 500 K and pressures near 50 bar), then it is possible to convert more than 55 % molar carbon of an aqueous sorbitol feed into hexane.<sup>[11]</sup>

The essential features of the above bifunctional reaction scheme (Scheme 7) for production of alkanes from sorbitol involve 1) hydrogen production on metal sites by cleavage of C–C bonds followed by the water gas shift reaction, 2) dehydration on acid sites, and 3) hydrogenation of the dehydrated species on metal sites. Repeated cycling of dehydration and hydrogenation reactions in the presence of  $\text{H}_2$  leads to heavier alkanes (such as hexane) from sorbitol. Formation of lighter alkanes takes place by cleavage of C–C bonds compared to hydrogenation of dehydrated reaction intermediates. Optimization of the aqueous-phase dehydration and hydrogenation (APD/H) system involves choosing

the proper metal catalyst, acid catalysts, ratio of metal-to-acid sites, reaction conditions, and proper reactor design.

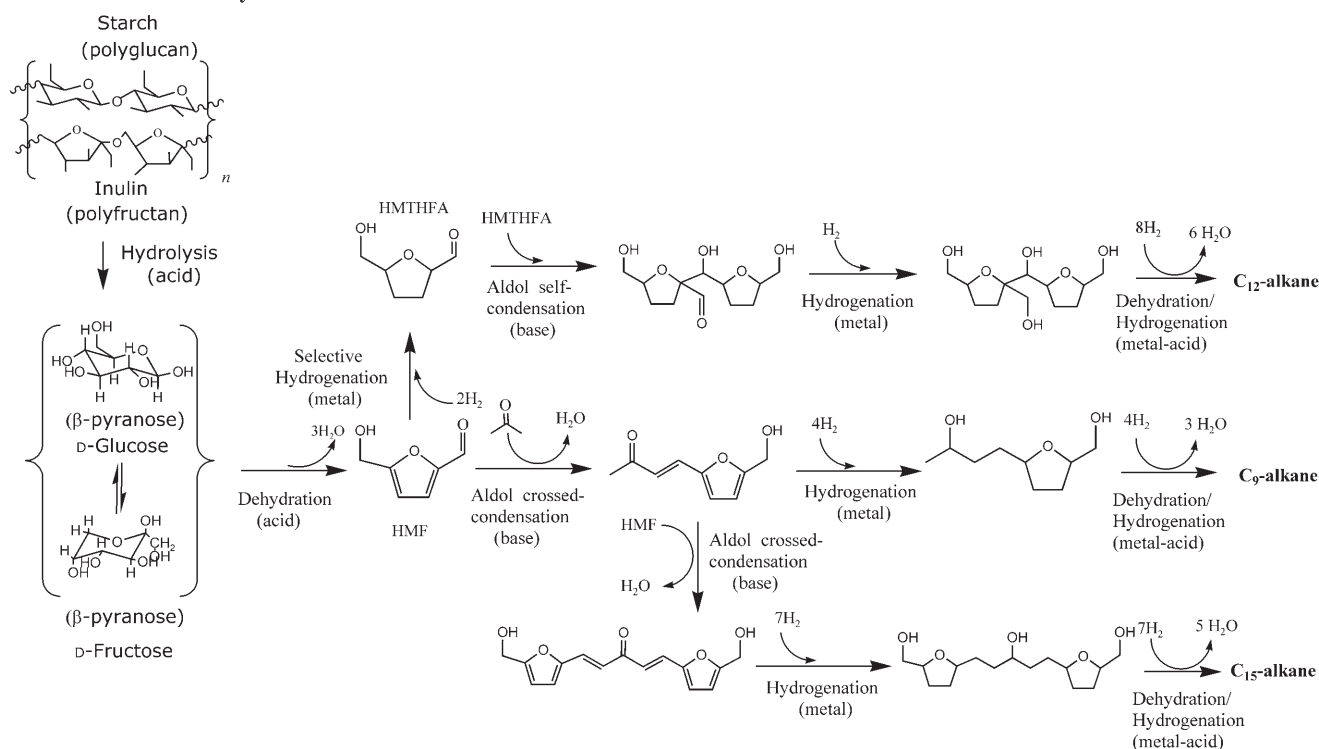
Whereas the aqueous-phase reforming step to produce  $\text{H}_2$  and  $\text{CO}_2$  is highly endothermic, the C–O hydrogenolysis and dehydration-hydrogenation processes are highly exothermic, such that the overall production of alkanes from carbohydrates is slightly exothermic, offering unique energy efficiency opportunities by the coupling of these endothermic and exothermic processes in a single reactor. As hydroxy groups are removed from the carbohydrate, the volatility of the feed increases and the energy density remains high. In particular, the alkanes retain more than 90 % of the energy content of the original carbohydrate feed, and they represent only 30 % of the original mass, leading to a high energy density. Moreover, as hydroxy groups are removed from the carbohydrate, the hydrophilic properties decrease and the hydrophobic alkane products separate spontaneously from water, thereby eliminating any energetically intensive distillation steps, such as those required for the separation of ethanol from water in the production of fuel-grade ethanol.

The alkanes produced in the APD/H process contain the same number of carbon atoms as the initial sugar (usually five or six carbon atoms), and hence they cannot be used directly for fuel applications owing to their high volatility. In general, however, it is desirable to produce longer-chain alkanes from biomass, thereby providing a renewable source of transportation fuel. In this respect, a process has recently been described that produces liquid alkanes, ranging from  $\text{C}_7$  to  $\text{C}_{15}$ , by aqueous-phase processing of biomass-derived carbohydrates.<sup>[8]</sup> The liquid alkanes ranging from  $\text{C}_5$  to  $\text{C}_9$  can complement the development of P-series fuel by substituting the pentane-plus components of this fuel,<sup>[18]</sup> and the oxygenated form of saturated molecules or heavier liquid alkanes ( $\text{C}_{13}$ – $\text{C}_{15}$ ) can serve as diesel-fuel additives. In addition, this 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.<sup>[75]</sup>

Production of heavier liquid-phase alkanes from carbohydrates involves a series of reaction steps starting with acid hydrolysis of polysaccharides such as cellulose, hemicellulose, starch, and inulin to produce monosaccharides such as glucose, fructose, and xylose (Scheme 8). Hydrolysis involves breaking of C–O–C linkages and is typically carried out in the presence of mineral acid catalysts. These carbohydrates can further undergo acid-catalyzed dehydration to form carbonyl-containing furan compounds such as HMF and furfural (as outlined in Section 5.2). Subsequently, these carbonyl-containing compounds can be coupled through an aldol condensation to produce larger organic molecules ( $> \text{C}_6$ ) by C–C bond formation. The reaction is typically carried out in polar solvents such as water or water-methanol in the presence of solid base catalysts, such as mixed Mg–Al oxides or  $\text{MgO-ZrO}_2$  at low temperatures. As indicated in Scheme 8, acetone forms an intermediate carbanion species that can cross-condense with HMF in the presence of a base catalyst to form  $\text{C}_9$  species, which can subsequently react with a second HMF molecule to form a  $\text{C}_{15}$  species. These aldol adducts have low solubility in water as a result of their nonpolar structure and



## Biomass-derived Carbohydrates



**Scheme 8.** Reaction pathways for the conversion of polysaccharides into liquid alkanes. Analogous chemistry can be depicted for the conversion of C<sub>5</sub> polysaccharides into C<sub>10</sub>, C<sub>8</sub>, and C<sub>13</sub> alkanes via furfural as reaction intermediate. (Adapted from Ref. [8].)

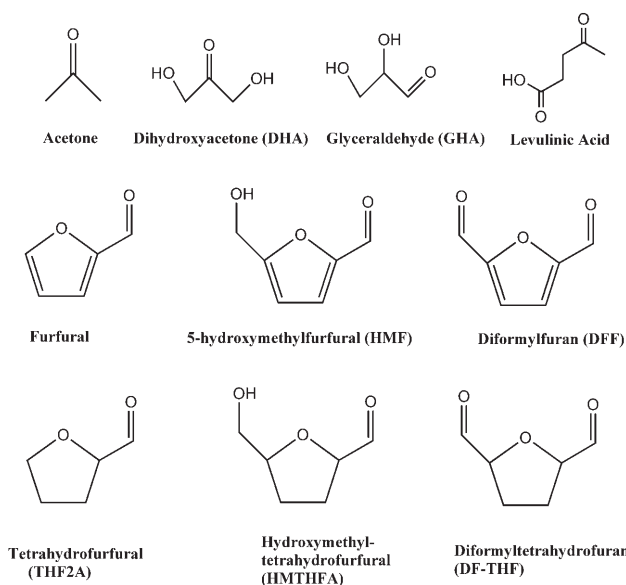
thus precipitate out of the aqueous phase. Subsequently, the C=C and C=O bonds in these aldol adducts are saturated by hydrogenation in the presence of a metal catalyst (Pd), thereby increasing their solubility and making large water-soluble organic compounds. These molecules are then converted into liquid alkanes (C<sub>7</sub>–C<sub>15</sub>) by aqueous-phase dehydration/hydrogenation (APD/H) over a bifunctional catalyst (Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) containing acid and metal sites in a four-phase flow reactor consisting of 1) an aqueous inlet stream containing large water-soluble compounds, 2) a hexadecane sweep inlet stream, 3) a H<sub>2</sub> gas inlet stream, and 4) a solid catalyst.<sup>[8]</sup> As dehydration/hydrogenation takes place, the aqueous organic reactants become more hydrophobic and the hexadecane sweep stream serves to remove hydrophobic species from the catalyst before they react further to form coke. The H<sub>2</sub> required for intermediate steps can be produced from sugars by using the APR process (as outlined in Section 5.1). Similarly, sugars can be fermented to form acetone or they can undergo retro-aldol condensation to form smaller carbonyl-containing compounds such as dihydroxyacetone and glyceraldehyde, which can be cross-condensed with furfural and HMF.

Another possible route for production of liquid alkanes is to convert HMF and furfural into 5-hydroxymethyltetrahydrofurfural (HMTHFA) and tetrahydrofurfural (THF2A), respectively, by 1) selective hydrogenation of the C=C bonds in the furan ring, 2) complete hydrogenation of these compounds followed by preferential dehydrogenation of the primary -C-OH group to form an aldehyde, or 3) complete hydrogenation followed by selective oxidation of the primary

-C-OH group upon reaction with O<sub>2</sub> to form an aldehyde. HMTHFA and THF2A can be self-condensed to form C<sub>12</sub> and C<sub>10</sub> species, respectively, that are subsequently hydrogenated to form water-soluble organic species. Overall, the intermediate steps for conversion of biomass into liquid alkane fuel 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. Importantly, the distribution of liquid alkanes from C<sub>7</sub> to C<sub>15</sub> can be controlled using the molar ratio of reactants such as HMF and acetone.<sup>[8]</sup>

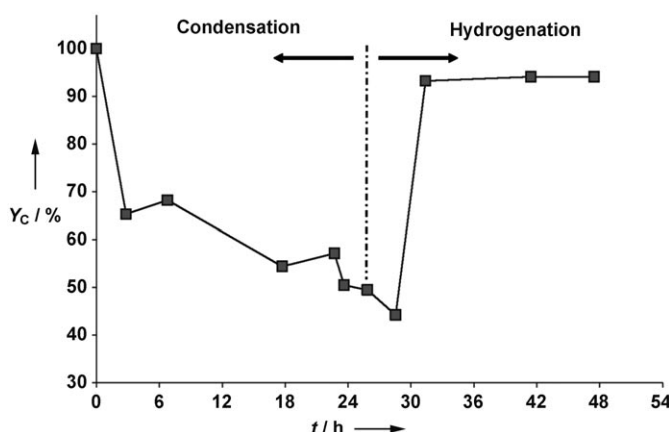
The aldol condensation is an important intermediate step to form large organic molecules using carbohydrate-derived carbonyl compounds. Even though sugars contain a carbonyl group, they undergo structural transformations in aqueous solution to form ring structures, resulting in less than 1 % of the acyclic form, thereby leading to low reaction rates for aldol condensation reactions.<sup>[30]</sup> As noted in Section 5.2, however, it is possible to dehydrate glucose, fructose, and xylose to HMF and furfural, respectively. More generally, Scheme 9 shows a variety of carbohydrate-derived oxygenated carbonyl compounds that can potentially be self- or cross-condensed to form larger organic molecules.<sup>[76]</sup>

In initial studies, aldol condensation reactions were carried out using a Mg/Al mixed oxide catalyst derived from hydrotalcite synthesis, and a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was subsequently added to carry out the hydrogenation step in a batch reactor. However, the mixed Mg/Al oxide catalyst lost almost 70 % of its activity upon subsequent recycling owing to



**Scheme 9.** Carbonyl compounds derived from carbohydrate feedstocks. (Adapted from Ref. [76].)

irreversible structural changes of the catalyst.<sup>[38]</sup> In subsequent studies, a magnesia-zirconia ( $\text{MgO-ZrO}_2$ ) catalyst was shown to be stable under aqueous-phase aldol condensation reaction conditions. During the aldol condensation reaction, the products precipitate out of the aqueous solution. Accordingly, Pd was deposited onto the  $\text{MgO-ZrO}_2$  catalyst to develop a bifunctional metal base ( $\text{Pd/MgO-ZrO}_2$ ) catalyst to facilitate a single-reactor design for aldol condensation and subsequent hydrogenation. Figure 4 shows the aqueous-phase



**Figure 4.** Overall carbon yield ( $Y_C$ ) in the aqueous phase versus time for aldol condensation of HMF with acetone (molar ratio of 1:1) at 326 K in the presence of 5 wt%  $\text{Pd/MgO-ZrO}_2$  catalyst followed by hydrogenation at 393 K. (Adapted from Ref. [38].)

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 using a bifunctional metal base catalyst ( $\text{Pd/MgO-ZrO}_2$ ) at 326 K, followed by hydrogenation in the same batch reactor at 393 K. As indicated in Figure 4, the carbon concentration in the

aqueous phase decreases due to insoluble products that precipitate out of the aqueous phase during aldol condensation. However, about 94 % of the initial carbon is recovered back in the liquid phase upon subsequent hydrogenation over the metal sites. Thus, the bifunctional  $\text{Pd/MgO-ZrO}_2$  catalyst allows an aqueous-phase process to be carried out that combines an aldol condensation with sequential hydrogenation in a single reactor, in which the carbon lost during the first step is returned to the aqueous phase during the hydrogenation step. The overall yield of heavier products ( $\text{C}_{13}\text{--C}_{15}$ ) can be adjusted by controlling the temperature and molar ratio of the reactants.<sup>[38]</sup>

## 6. Summary and Outlook

Biomass, and particularly lignocellulosic biomass, is an abundant and sustainable source of carbon for the production of fuels and chemicals. To develop processes for the efficient utilization of biomass resources, it is important to understand carbohydrate chemistry and how catalysts can be used to alter the high degree of oxygen functionality of these molecules. While a wide variety of products can be formed from carbohydrates, these products are typically formed from fundamental reactions including hydrolysis, dehydration, isomerization, aldol condensation, reforming, hydrogenation, and oxidation. These key reaction pathways can be combined using multifunctional catalysts to produce an even wider range of products from carbohydrate-based feedstocks.

Understanding critical requirements for each of the aforementioned fundamental reactions can help to identify unique opportunities for developing cost-effective processing methods. For example, we have shown that by controlling the reaction conditions and the nature of the catalyst it is possible to use aqueous-phase reforming of polyols to produce primarily  $\text{H}_2$  and  $\text{CO}_2$  or to produce  $\text{H}_2$  and CO (synthesis gas) over metal and metal-alloy catalysts. Alternatively, it is possible to carry out aqueous-phase processing of sorbitol to produce light alkanes ( $\text{C}_1\text{--C}_6$ ) using a bifunctional catalyst, where the metal component catalyzes the aqueous-phase reforming of sorbitol to produce  $\text{H}_2$ , and the acid constituent catalyzes dehydration of sorbitol to form intermediate species that can be further hydrogenated (by the metal component) to form alkanes. We have also shown how fructose can be selectively dehydrated to form HMF in high yields (> 90 %) using a biphasic reactor system that has a reactive aqueous phase, which contains catalyst and sugar modified by adding promoters to suppress side reactions. The HMF product is continuously extracted into an organic phase modified to enhance the partitioning from the aqueous phase, thereby providing a cost-effective means to produce HMF. This biphasic reactor system can be fine-tuned to produce furfural and HMF from polysaccharides by controlling the reaction conditions and by adjusting the concentrations of reaction modifiers to achieve hydrolysis of the polysaccharides combined with dehydration of the resulting monosaccharide species. We have also discussed how carbohydrates can be converted into liquid alkanes using a multistep catalytic process, involving dehydration, aldol condensation, hydro-

genation, followed by dehydration/hydrogenation. These examples illustrate that many possibilities exist for reacting carbohydrates and carbohydrate-derived compounds using multifunctional catalysts to form value-added chemicals and fuels. While many challenges are involved in carbohydrate processing, this area of research also provides a wide range of opportunities to develop innovative processing technologies.

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