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Review

Production of Fuels and Chemicals from Biomass: Condensation Reactions and Beyond

Lipeng Wu,¹ Takahiko Moteki,² Amit A. Gokhale,³ David W. Flaherty,^{2,*} and F. Dean Toste^{1,*}

Renewable resources and bio-based feedstocks may present a sustainable alternative to petrochemical sources to satisfy modern society's ever-increasing demand for energy and chemicals. However, the conversion processes needed for these future bio-refineries will likely differ from those currently used in the petrochemical industry. Biotechnology and chemocatalysis offer routes for converting biomass into a variety of molecules that can serve as platform chemicals. While a host of technologies can be leveraged for biomass upgrading, condensation reactions are significant because they have the potential to upgrade these bio-derived feedstocks while minimizing the loss of carbon and the generation of by-products. This review surveys both the biological and chemical catalytic routes to producing platform chemicals from renewable sources and describes advances in condensation chemistry and strategies for the conversion of these platform chemicals into fuels and high-value chemicals.

INTRODUCTION

Over the past few decades, improved public awareness of the links between climate change and anthropogenic greenhouse gas (GHG) emissions has increased political will around the world to tackle this problem and the demand for renewable products.¹ In parallel, advancements in agronomic and biological technologies have improved plant output and created greater amounts of renewable feedstocks. Commercial considerations have identified sugars from sugarcane, sugar beets, grain starches (e.g., corn and wheat), and lignocellulose, as well as vegetable oils from palm, soybean, and oilseeds, as promising feedstocks for upgrading. However, new conversion processes are needed to improve chemical and thermal properties and increase the energy densities of these feedstocks if they are to replace those derived from petroleum.

The volatility of the energy markets over the past decade inspired innovations in bioscience and chemistry that have resulted in a range of renewable alternatives for fuels and chemicals. Today, biotechnology offers routes for converting biomass into a variety of functional moieties (e.g., alcohols, alkenes, ketones, acids). Similarly, a plethora of possibilities are available through heterogeneous and homogeneous chemocatalysis, including reactions of sugars and even complex lignocellulosic materials to yield mixtures of platform chemicals.² An alternative strategy³ leverages both biology and chemocatalysis by deploying biotechnology (fermentations) to produce platform chemicals that are chemically transformed into fuels and other high-value chemicals.⁴ While a host of different reactions have been used for biomass upgrading, condensation reactions, such as aldol condensation, etherification, ketonization, and esterification, are particularly significant chemical transformations, because they allow for the upgrading of bio-derived feedstocks

The Bigger Picture

Sustainability of society is intimately tied to the utilization of renewable resources to meet the demand for energy and chemicals. Bio-based feedstocks may present a greener route to satisfy these demands, but the conversion processes used in future bio-refineries will differ from those in the petrochemical industry. Such processes may breakdown sugars, their oligomers, and other biomass components into simple molecules that functionally resemble petroleum-derived intermediates. Thus, the portfolio of fossil and biomass building blocks may intertwine and be upgraded into useful chemicals. Developments in homogeneous and heterogeneous catalysis have fueled the search for effective approaches to utilizing renewable sources; however, further advances are needed to realize technologies that are competitive with established petrochemical processes. Catalysis will play a key role, with new reactions, processes, and concepts that leverage both traditional and emerging chemo- and bio-catalytic technologies.

while minimizing the loss of carbon and the generation of by-products. In this review, we explore the utility of such condensation reactions for promoting biomass-derived platform chemicals into fuels and chemicals. We begin by surveying both biological and chemical catalytic routes to produce platform chemicals from renewable sources. We then describe recent advances in condensation chemistry and strategies inspired by these advances for the conversion of these platform chemicals into fuels and high-value chemicals.

PRODUCTION OF BUILDING BLOCKS

In order to produce fuels and chemicals, several currently available processes rely on entirely breaking down complex molecules before building up the desired compounds, such as the case with syngas production, to form alkanes and alcohols. While biomass can also be converted into syngas, an alternative and complimentary approach strategically converts biomass into chemical building blocks that retain features (e.g., electrophilic or nucleophilic character) that can be exploited in further manipulations. Such platform chemicals can be generated through either chemical routes or biological processes. In this section, we highlight and compare these strategies for production of biomass-derived renewable products with routes based on petroleum feedstocks.

Alcohols: Ethanol, Butanol, and Higher Alcohols

The emergence of low-cost oil in the 1900s and the formation of the petrochemical industry led to ethanol production via acid-catalyzed hydration of ethylene. However, a combination of regulatory frameworks, technological advances, and market factors led to the resurgence of ethanol production from renewable sugars over the past few decades, with the result that nearly 90% of ethanol is now derived from biomass.⁵ Most ethanol is produced from sugar (e.g., starch from maize grains or sucrose from sugarcane) fermentation using the yeast species *Saccharomyces cerevisiae*. Recent efforts have pushed to replace edible sugars with lignocellulosic biomass (e.g., corn stover) as feedstocks, which may reduce the cost of bioethanol and decrease GHG emissions simultaneously.⁵

1-Butanol may be produced from syngas via methanol and subsequent alcohol homologation; however, the currently favored route involves regioselective rhodium-catalyzed hydroformylation of propylene to *n*-butyraldehyde followed by hydrogenation to 1-butanol (Scheme 1A).⁶ Alternatively, 1-butanol may be produced by microbial fermentation using organisms such as *Clostridium acetobutylicum*, which provides mixtures of acetone, 1-butanol, and ethanol (ABE fermentation), or other species that produce 1-butanol exclusively.⁷ The Guerbet reaction of bioethanol, which is more easily produced by fermentation and separated at higher titers, provides an alternative route for 1-butanol production (Scheme 1B).

The hydrogenolysis of renewable triglycerides derived from vegetable oils offers a pathway to desirable C₈₊ alcohols. At high H₂ pressures, Zn- and Cu-based heterogeneous catalysts reduce both carboxylic groups as well as C=C bonds in unsaturated fatty acids and esters to give a range of higher alcohols (Scheme 1C).¹ Alcohols can also be generated from fatty acids by oxidative cleavage using Ru, Os, or Pd catalysts and oxidants such as O₃, NaIO₄, or H₂O₂.⁸ The resulting shorter-chain aldehydes and acids can be readily hydrogenated to form the desired alcohols (Scheme 1D).

Aliphatic Acids

A number of valuable aliphatic acids can be produced either by biological or chemical pathways.⁹ Acetic acid is produced both by chemical synthesis and by fermentation processes. Industrially, 75% of acetic acid is produced from methanol

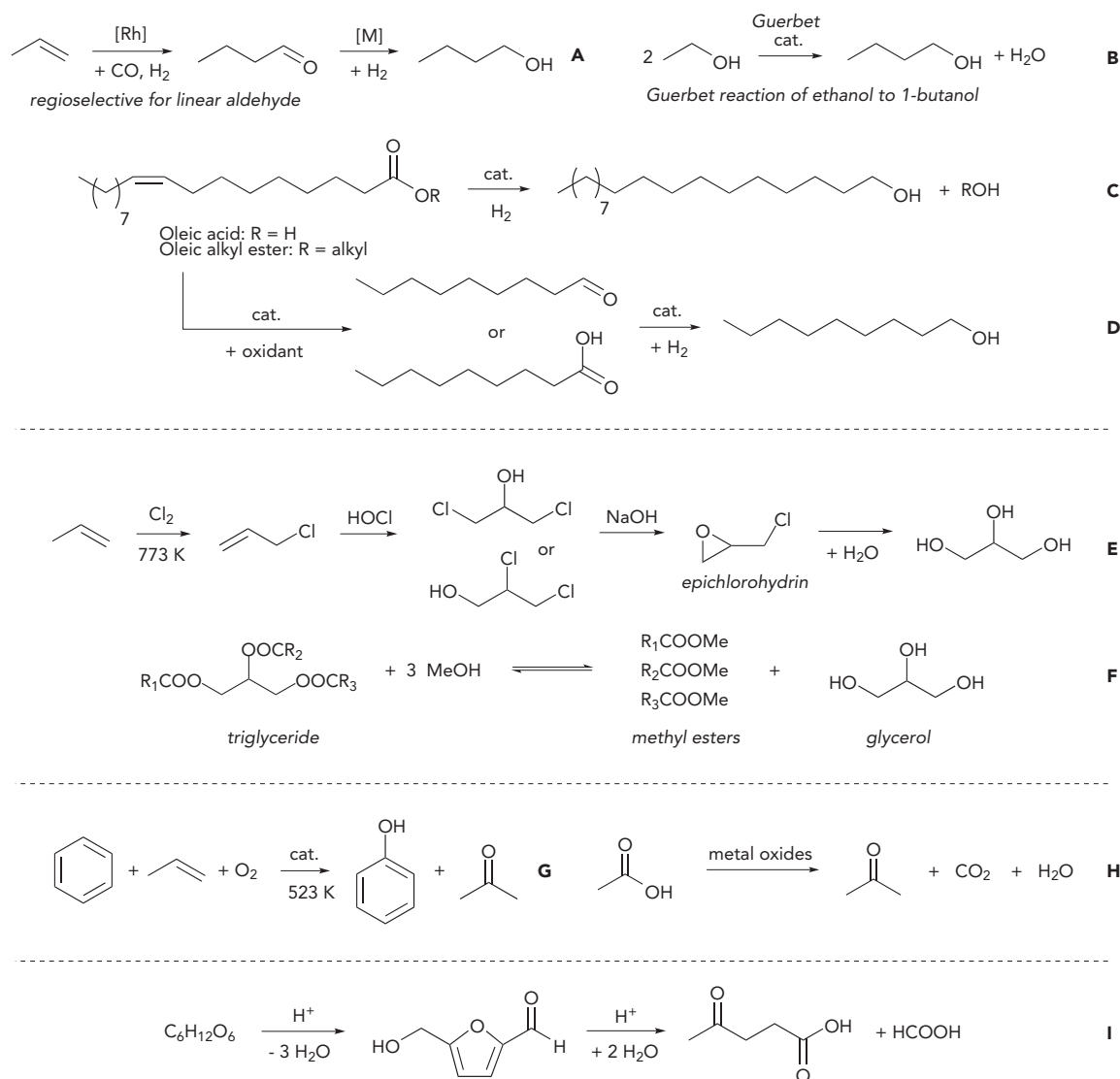
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Scheme 1. Production of Platform Chemicals from Fossil and Renewable Sources

- (A) Hydroformylation of propylene to aldehyde and then hydrogenation to alcohol.
 (B) Guerbet reaction of ethanol to 1-butanol.
 (C) Direct hydrogenation of fatty acid or its ester to fatty alcohol.
 (D) Oxidative cleavage of fatty acid to aldehyde or acid and reduction to alcohol.
 (E) Epichlorohydrin process to produce glycerol from propylene.
 (F) Glycerol production from transesterification of triglyceride.
 (G) Cumene oxidation process to produce acetone.
 (H) Ketonization of acetic acid to acetone.
 (I) Levulinic acid from hexose.

carbonylation using the Rh-catalyzed Monsanto process or the Ir-catalyzed Cativa process.¹⁰ In bio-catalytic processes, acetic acid is produced either by oxidative fermentation of ethanol using *Acetobacter* or via the direct fermentation of sugar to acetic acid. Longer aliphatic acids arise from the hydrocarboxylation reaction of alkenes with carbon monoxide and water in the presence of Pd or Ni catalysts. Alternatively, the aliphatic alcohols or aldehydes generated by the pathways described above can be oxidized to the corresponding acids with air using cobalt or

magnesium catalysts. Longer fatty acids are available from the hydrolysis of triglycerides, with the removal of glycerol. Another important acid used in the industry is lactic acid, and this can be produced synthetically by the chemical hydrolysis of lactonitrile using strong acids. Alternatively, renewable substrates such as glucose, sucrose, lactose, or other sugars may be used as feedstocks for fermentation processes employing *Lactobacillus* strains to give lactate from which lactic acid may be recovered.¹¹ Finally, diacids are useful in the polymer industry, and fermentation processes using engineered *Escherichia coli* or other organisms are being developed to produce C₄ and C₆ diacids (e.g., succinic acid production from lignocellulosic material fermentation).¹²

Glycerol

Glycerol can be produced either from oxidations of light petroleum derivatives or from biomass via transesterification of triglycerides from fats and oils. Synthetic glycerol is produced conventionally from propylene by sequential chlorination to form allyl chloride, addition of hypochlorous acid followed by base to give epichlorohydrin, and final hydrolysis producing glycerol (Scheme 1E).¹³ Transesterification of triglycerides with alcohols (e.g., methanol, ethanol) in the presence of acid or base catalysts gives glycerol and fatty acid esters (Scheme 1F).¹ Base catalysts give higher rates than acid catalysts; however, bases increase the difficulty of separating glycerol from the aqueous phase within the reactor. High-purity glycerol (>99.5%) can be produced using a series of separation processes (e.g., extraction, neutralization, and distillation). Alternatively, glycerol can be obtained as a by-product from the fermentation of glucose and fructose into ethanol (e.g., using *Saccharomyces cerevisiae*).¹⁴

Acetone

The petrochemical industry has developed multiple processes to produce acetone; however, the cumene oxidation process accounts for nearly 90% of the acetone produced today. This process involves the reaction of benzene with propylene in the presence of oxygen and a phosphoric acid or zeolitic solid acid catalyst to produce acetone and phenol (Scheme 1G).¹⁵ Alternatively, acetone can be produced by decarboxylative ketonization of acetic acid, catalyzed by a number of dispersed metal oxides (e.g., CeO₂, MgO, MnO₂, CdO, and La₂O₃) (Scheme 1H).¹⁶ Finally, ABE fermentation of sugars produces acetone (along with butanol and ethanol) as mentioned above.⁴

Furans and Levulinic Acid

Furfural can be produced either as an exclusive product or as a co-product from lignocellulose bio-refineries. The dehydration of xylose (C₅ sugar) to furfural in water proceeds over a wide range of temperatures (423–493 K) and gives furfural yields of 60%–70% under stripping conditions.¹ The dehydration of hexoses (C₆ sugars) via fructose intermediates produces 5-hydroxymethylfurfural (HMF) with considerably higher yields of HMF than that from glucose (Scheme 1I). HMF is a very active intermediate, and its relatively high boiling point makes it hard to separate from aqueous solutions. Several process options, from pervaporation to in situ liquid extraction and etherification, have been implemented to arrest the degradation of HMF to levulinic acid (LA) and its polymerization.

LA is formed by the dehydration of hexoses to HMF and the subsequent hydration of HMF to generate equimolar quantities of LA and formic acid (Scheme 1I). Alternatively, the furfural produced from pentose can be transformed further into LA by subsequent hydrogenation to furfuryl alcohol and hydrolysis to LA.¹ The ketone

and carboxylic acid functionality in LA makes it a desirable intermediate for the production of long-chain molecules.

ESTABLISHED CONDENSATION REACTIONS FOR BIOMASS UPGRADING

Condensation reactions and subsequent transformations of platform chemicals (e.g., alcohols, aldehydes, and ketones) provide facile methods to construct larger products with structures, functionalities, and physical properties that are desirable for use as transportation fuels or specialty chemicals. Aldol condensation, acetalization, etherification, esterification, and ketonization are among the most studied condensation reactions.

Aldol Condensation

Aldol condensation is one of the most powerful reactions that form C–C bonds. The extent of the addition reaction of two species containing carbonyl groups to form aldol adducts is controlled by equilibrium; however, dehydration is highly favorable and drives the reaction forward to form the α,β -unsaturated aldehyde. Aldol condensations are especially useful in biomass upgrading because the facile dehydration removes oxygen, increases the carbon to oxygen ratio, and assists in the conversion of biomass-derived oxygenates to liquid hydrocarbons. Therefore, this coupling reaction is widely used to upgrade bio-derived carbonyl compounds to form larger products that can be converted into jet and diesel fuels or lubricants by subsequent hydrogenation.⁴

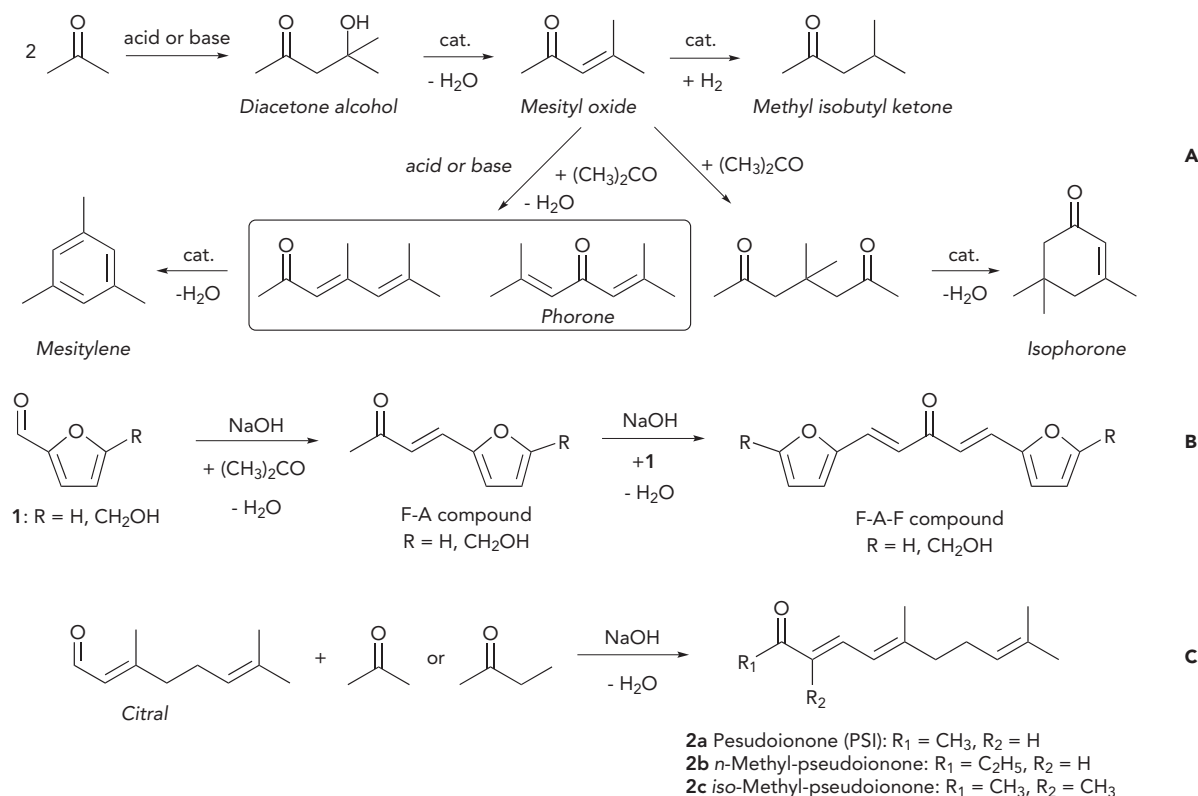
Aldol condensations are generally carried out at mild reaction temperatures (273–473 K) in the presence of a homogeneous or heterogeneous acid, base, or amphoteric catalyst (e.g., alkali metals,^{17–21} metal oxides,^{18–20,22–24} mixed metal oxides,^{19,23,25–29} hydroxyapatite,^{23,24,30} amines grafted onto supports,³¹ and metal-substituted zeolites^{23,24}). Recent improvements in heterogeneous catalyst systems possessing acid-base bifunctionality showed greater reaction rates by stabilizing the transition states on the acid-base pair sites. Factors such as reaction temperature,^{18,19,25} reactant molar ratio,^{21,29,32–34} structure of reactant molecules,^{27,29} and the nature of the catalyst^{29–31} determine the selectivity of the process toward heavier compounds.

Aldol Condensations of Aldehydes

Liquid- and vapor-phase aldol condensation of light aldehydes (C_2 – C_4) have been studied in the past decades over a number of catalysts (solid base, acid, acid-base bifunctional catalysts, and redox catalysts). The most frequently studied reaction is the self-condensation of acetaldehyde to form crotonaldehyde. Ji et al.¹⁸ reported selectivities of 90% for the formation of crotonaldehyde over silica-supported alkali metals. Recently, Rekoske and Barteau²² demonstrated the highly selective (~100%) production of crotonaldehyde from acetaldehyde over TiO_2 at 523 K. Aldol condensation is also used to produce 2-ethyl-hexanal from *n*-butyraldehyde. These products are frequently hydrogenated using either external H_2 or catalytic transfer hydrogenation from alcohols to form saturated alcohols that are useful as diesel additives, flavors, or building blocks for plasticizers.⁶ Importantly, aldol condensation of aldehydes is a critical step in the Guerbet reaction (described later in this review) and efficiently builds high-molecular-weight branched alcohols.²⁴

Aldol Condensation of Ketones

Catalytic self-aldol condensation of acetone is a complex reaction and numerous products are possible via competitive self- and cross-condensation between the reactants and primary products (Scheme 2A).¹⁹ Self-aldol condensation of acetone



Scheme 2. Aldol Condensation Reactions of Different Aldehydes and Ketones

(A) Self-aldol condensation of acetone.

(B) Aldol condensation of furfural with acetone.

(C) Aldol condensation of citral with ketones.

initially forms diacetone alcohol (DAA) as an aldol product, but in order to obtain high yields of DAA, the condensation reaction must be stopped before DAA reacts further. Thus, catalytic conversion of acetone to DAA is most effective at low temperatures (273–293 K) whereby the extent of the reaction over basic hydroxide, oxide, carbonate, or metal catalysts can be controlled.¹⁹ Subsequent dehydration of DAA forms mesityl oxide (MO), which is obtained in good yield at mild reaction temperatures (293–473 K). Methyl isobutyl ketone is formed by selective hydrogenation of MO.¹⁹

At higher temperatures (>473 K), aldol condensation of acetone shows more complex reaction pathways and yields acyclic, cyclic, and aromatic trimers (phorones, isophorone, and mesitylene, respectively) (Scheme 2A).^{19,20,25} Generally, phorone yields are low because acidic condensation catalysts also promote coupled cyclization and dehydration reactions that produce mesitylene, the thermodynamically favored product at higher temperatures and pressures.¹⁹ Mesitylene itself is a useful chemical and is known to have a high octane number; however, the relatively high cost of producing mesitylene limits its use as fuel except in niche applications such as aviation gasoline. Trimerization of acetone under basic conditions produces isophorone (Scheme 2A),²⁰ a potential intermediate to form 3,5-xyleneol. Selectivities to C₉ products from the self-condensation of acetone using Mg-Zr oxides can surpass 50% at higher temperatures, whereas MO (C₆) is the predominant product (>85% selectivity) at lower temperatures.²⁵ Along with isophorone, acetone

condensation also tends to give significant amounts of C₁₂ and C₁₅₊ compounds because of the high reactivity of the intermediates.

In contrast, C \geq 4 alkyl methyl ketones can undergo selective reaction at the methyl group; consequently on base catalysts such as hydrotalcite, such methyl ketones yield primarily trimeric products. Hydrogenation of aldol condensation products yields jet fuels and lubricants, as demonstrated by recent studies from the Toste and Bell groups.²⁷ While trimers of methyl ketones can act as precursors for jet fuels, diesel precursors are generally composed of relatively linear structures and therefore would require stopping the reaction after dimerization. Kunkes et al.²⁶ have demonstrated that Pd-supported on CeZrO_x catalyzed the dimerization of 2-hexanone with selectivities greater than 95% at 313 K. Similarly, amine-modified silica alumina catalysts are also effective for the selective dimerization of biomass-derived methyl ketones (C₄–C₁₅).³¹

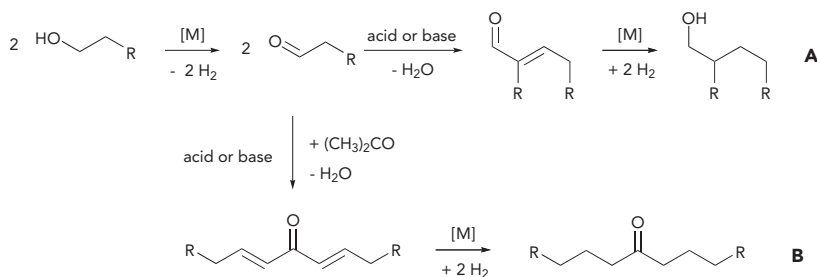
Aldol Condensation of Furanics and Acetone

The aldol condensation of biomass-derived furanic compounds containing carbonyl functions (e.g., furfural, HMF, or tetrahydrofurfural) with ketones can be used to produce long-chain hydrocarbons.³⁵ This approach initially generates larger cyclic ethers that are subsequently hydro-treated to open rings, remove oxygen, and saturate the final products. Pioneering efforts produced C₇–C₁₅ alkanes appropriate for diesel and jet fuel from condensation of furanics with acetone (Scheme 2B).³⁵ Such a reaction produces a narrow distribution of products because condensation occurs only when the acetone enolate ions attack the aldehyde of the furanic compound to produce a furan-acetone (F-A) adduct (Scheme 2B). Ketones with two reactive α -carbon atoms to the carbonyl can undergo a second condensation with the furanic co-reactant to produce F-A-F compounds (Scheme 2B). The low solubility of such aldol condensation products in pure water can be exploited as a strategy for recovering the products by simple phase separation.

The distribution between single (F-A) and double (F-A-F) condensation products depends largely on the initial molar ratio of furfural to ketone reactants.²¹ A high ratio of ketones to furanics favors the formation of monomers (F-A), whereas a low ratio favors dimer (F-A-F) production.²¹ Because of the complementary functionalities of furanics and ketones, product selectivity does not depend strongly on parameters such as the reaction temperature or the method by which the reactants are combined (e.g., stepwise addition of acetone).³² While hydrogenation of the F-A and F-A-F compounds can give diesel-range compounds, we anticipate that some of these adducts might also be used to prepare high-value chemicals. For example, 2,5-furandicarboxylic acid has been suggested as a suitable monomer for producing polyesters,³⁶ and therefore F-A-F type compounds produced from HMF, upon oxidation, could find similar applications.

Aldol Condensations of Citral with Acetone

Aldol condensation of citral with acetone or methyl ethyl ketone (MEK) forms pseudoionones (PIs), which are acyclic precursors to ionones and methylionones (Scheme 2C). PIs and ionones are important intermediates in the production of pharmaceuticals, fragrances, and vitamin A. During these reactions, the enolate of acetone attacks the carbonyl group of citral. Heterogeneous catalysts (e.g., MgO, HT, or KF/Al₂O₃) are used at low temperatures (273–353 K) to prepare PIs with selectivities \sim 90% and yields of 60%–80%.³⁷ The yield losses result primarily from the undesirable self-condensation of citrals or ketones and secondary reactions of PIs.



Scheme 3. Reactions Involved in Aldol Condensation

(A) Guerbet reaction of alcohols.

(B) Aldol condensation of acetone with alcohols.

Selective conversion of citral depends strongly on the molar ratio of the reactants, as shown by selectivities and rates of PI and methyl-PI formation from reactions of citral with acetone and with MEK, respectively.²⁹ During methyl-PI production, condensation through either the methyl or the methylene group gives different isomeric products. Overall, yields of *n*-methylpseudoionone are greater than those for *iso*-methylpseudoionone because of the higher acidity of the methyl group and the greater steric hindrance of the ethyl group compared with the methyl group.²⁹

Alcohol Coupling Reaction via Aldolization: The Guerbet Reaction

The Guerbet reaction effectively forms 1-butanol or larger alcohols with unique branching patterns from the condensation reaction of two smaller primary alcohols (e.g., ethanol, 1-butanol or C \geq 3 alcohols) to *iso*-alcohols) via aldol condensation reactions between aldehyde intermediates.^{17,23,24} Much of the past work focused on upgrading bio-derived ethanol to 1-butanol,^{23,24} although the reaction has also been used to produce surfactants and lubricant precursors by forming larger alcohols.¹⁷

The Guerbet reaction is thought to involve an intermediate aldol condensation step coupled with alcohol hydrogen-transfer reactions (Scheme 3A). Several observations support this idea, including the direct observation of aldehyde and enal intermediates, the promotion of the reaction by addition of carbonyl species, and the formation of certain α -alkyl branching alcohols.^{23,24} The commonly accepted mechanism includes three steps: alcohol dehydrogenation, aldol condensation, and enal hydrogenation to form a saturated alcohol.^{23,24} Dehydrogenation of the reactant alcohols is frequently rate determining, especially when lower temperatures or higher H₂ pressures are used. Depending on the identity of the catalyst, the H atoms can either be liberated as H₂ or persist on the catalyst until reaction with unsaturated intermediates. Even with the use of metal dehydrogenation catalysts, the condensation reaction rates can be increased by directly adding aldehyde reactants to the system.

Guerbet chemistry has been explored as a pathway to upgrade C₁–C₅ alcohols derived from fermentation over heterogeneous catalysts. MgO is frequently used because of its high reactivity and selectivity. MgO by itself can catalyze the reaction; however, transition metals (e.g., Cu, Ru, Pd, and Pt) can be added to the system to promote the hydrogen-transfer reactions. Catalysts possessing acid-base bifunctionality are also effective for this reaction, such as Mg/Al mixed oxides derived from hydrotalcite and the non-metal oxide, hydroxyapatite. 1-Butanol selectivities of 70% are reported for ethanol coupling at conversions up to 20% over hydroxyapatite,³⁰ which has motivated interest in using the Guerbet reaction as a route for producing 1-butanol. Coupling of 1-butanol to give 2-ethylhexanol (2-EH) is also

of interest. Commercially, 2-EH is produced from propylene and is used extensively in plasticizers. Renewable 2-EH may be produced efficiently by catalytic conversion of 1-butanol produced by fermentation.⁷ Homogeneous catalysts such as NaOH or KOH catalyze the self-condensation of linear fatty alcohols in liquid solvents to form larger alcohols (C₁₆–C₂₄).¹⁷ However, water produced during the reaction inhibits such catalysts and must be continuously removed to achieve acceptable conversions and selectivities. Nevertheless, it is possible to remove the water formed in the process using suitable engineering techniques (e.g., reactive distillation), and such reactions could produce Guerbet alcohols from smaller bio-derived alcohols for use in the detergents and lubricant industries.

Aldol Condensation of Alcohols with Acetone and Other Methyl Ketones

Condensation of alcohols with acetone is of particular importance for increasing the chain length of biomass-derived products. Mechanistically, the reaction proceeds via dehydrogenation of alcohols to give aldehydes, which undergo condensation with acetone to form an intermediate that on hydrogenation can give linear or branched ketones depending on the reactant alcohol (Scheme 3B).⁴ Hydrodeoxygenation of the ketones obtained from reaction of acetone with alcohols (C₈–C₁₆) gives compounds that are structurally similar to diesel-range compounds and to those used in oilfield chemicals. Interestingly, the same scheme, when used in conjunction with long-chain Guerbet alcohols, can facilitate the production of renewably sourced synthetic lubricant base oils. Hydrodeoxygenation of products obtained through aldol condensation of these alcohols with acetone or methyl ketones gives compounds with structures comparable with oligomers of 1-decene that are currently used in automotive and industrial lubricants.³⁸

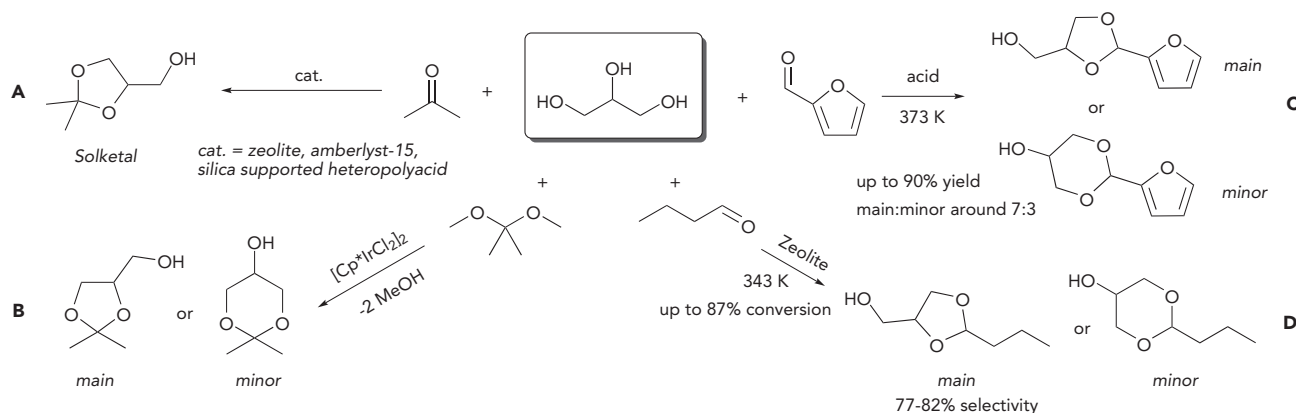
Retro-aldol Reaction of Sugars to Aldehydes

Aldol condensations are reversible, and the retro-aldol reaction breaks C–C bonds adjacent to carbonyl groups. The retro-aldol reaction selectively hydrolyzes heavier sugars (e.g., disaccharides and hexose) into lighter sugars (e.g., diose, triose, and tetrose). Subsequent hydrogenation can be used to form platform chemicals, including ethylene glycol or lactic acid derivatives.^{39,40} Retro-aldol reaction of glucose produces glycol aldehyde (C₂) and erythrose (C₄), whereas that of fructose gives glyceraldehyde (C₃) and dihydroxyacetone (C₃). Further, retro-aldol can cleave erythrose into additional two molecules of glycolaldehyde.³⁹ These C₂–C₄ species may also be obtained by reactions of polyols (e.g., sorbitol) and other carbohydrates.³⁹ Ni-promoted tungsten carbide (W₂C) catalysts have been used in the selective one-pot production of ethylene glycol from cellulose with yields in excess of 60%.⁴⁰ In general, a high selectivity to a specific product requires an appropriate sugar and careful tuning of the catalyst and reaction condition to facilitate cleavage of the desired C–C bond.

Acetalization

Acetalization involves the formation of acetals (or ketals) from an alcohol or ortho-ester with carbonyl compounds (e.g., ketones or aldehydes) in the presence of an acid catalyst. Decades of work has shown that glycerol, obtained from hydrolysis of fats, reacts with carbonyl compounds to produce mixtures of cyclic acetals consisting of six-membered ([1,3]dioxin-5-ols) and five-membered ([1,3]dioxolan-4-yl-methanols) rings.⁴¹ Such glycerol-derived cyclic acetals are valuable chemicals that can be used as additives for diesel fuels and as building blocks for surfactants.

The distributions of these products depend sensitively on the choice of catalyst, reaction conditions, and substrate. The acetalization of glycerol with carbonyl compounds including benzaldehyde, formaldehyde, and acetone shows selectivity



Scheme 4. Cyclic Acetals from Acetalization of Glycerol with Carbonyl Compounds

(A) Acetalization of glycerol with acetone.

(B) Transacetalization of 2,2-dimethoxypropane with glycerol.

(C) Acetalization of glycerol with furfural.

(D) Acetalization of glycerol with *n*-butyraldehyde.

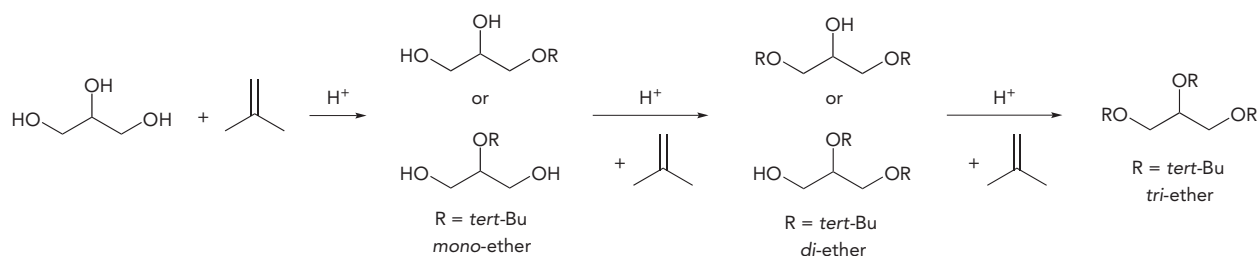
trends that differ remarkably.⁴¹ The reaction of glycerol with benzaldehyde gives a nearly 1:1 mixture of five- and six-membered rings over the acidic resin Amberlyst-36, whereas reaction with formaldehyde forms the six-membered cyclic acetal with 78% selectivity. In contrast, acetalization with acetone exclusively produces the five-membered cyclic acetal, solketal (4-hydroxymethyl-2, 2-dimethyl-1, 3-dioxolane) (Scheme 4A).⁴¹ The addition of 1–5 vol % solketal to gasoline improves the octane number and leads to a significant decrease in gum formation, which suggests that it possesses beneficial anti-oxidation properties.

Reaction with Acetone

The reaction of glycerol with acetone produces solketal with near perfect selectivities;⁴² however, this reaction requires severe conditions and exhibits slow rates even with strong acid catalysts (e.g., sulfuric, hydrochloric, or *p*-toluenesulfonic acids). These difficulties have been traditionally addressed by performing the reaction in batch mode within a Dean-Stark apparatus to remove water and shift the equilibrium toward solketal. Notably, Clarkson et al.⁴³ developed a continuous-flow process to produce solketal with 97% selectivity at 343 K using Amberlyst DPT-1 as the catalyst. Interestingly, this approach also gave similar results using wet glycerol (20 wt % in water), albeit at slightly higher temperatures. In addition, silica-supported heteropolyacids (e.g., tungstophosphoric, molybdophosphoric, tungstosilicic, and molybdosilicic acids) catalyzed the acetalization of glycerol with acetone. Homogeneous catalysts are also effective for transacetalization reactions of glycerol such as $[\text{Cp}^*\text{IrCl}_2]_2$, which gives a turnover number (TON) over 1,400 for the transacetalization of glycerol with 2,2-dimethoxypropane (Scheme 4B).⁴⁴

Reaction with Aldehydes

Acetalization of furfural with glycerol has been demonstrated, mostly with continuous water removal from refluxing organic solvents. Wegenhart et al.⁴⁵ reported yields up to 90%, notably without a water separation apparatus, using both homogeneous Lewis acid (ZnCl_2 , CuCl_2 , $\text{Cu}(\text{OTf})_2$, AlCl_3 , NiCl_2 , AgOTf , AgBF_4) and heterogeneous acid catalysts (aluminosilicate MCM-41 [Al = 3%] and Montmorillonite K-10 clay) (Scheme 4C). Longer reaction times were needed for heterogeneous catalysts; however, these materials were recovered and reused without a discernible loss of activity.



Scheme 5. Etherification of Glycerol with Isobutylene

Acetalization of glycerol with benzaldehyde was carried out using a series of MoO₃/SiO₂ catalysts with varying MoO₃ loadings (1–20 mol %).⁴⁶ Not surprisingly, the catalyst with the highest MoO₃ loadings (20 mol %) gave the greatest conversion of benzaldehyde (72%) but also showed 60% selectivity to the six-membered acetal at 373 K.⁴⁶ Acetalization of glycerol with *n*-butyraldehyde was investigated on a series of zeolites with different frameworks (faujasite, beta, and ZSM-5) and acidity (e.g., Si/Al ratio).⁴⁷ All zeolitic catalysts gave high selectivity to the five-membered ring acetal product (77%–82%) (Scheme 4D). The optimum Si/Al ratio was 30 for FAU; however, β -zeolite presented the highest catalytic activity among all zeolites, potentially due to more rapid diffusion through the larger pores of *BEA.

Etherification

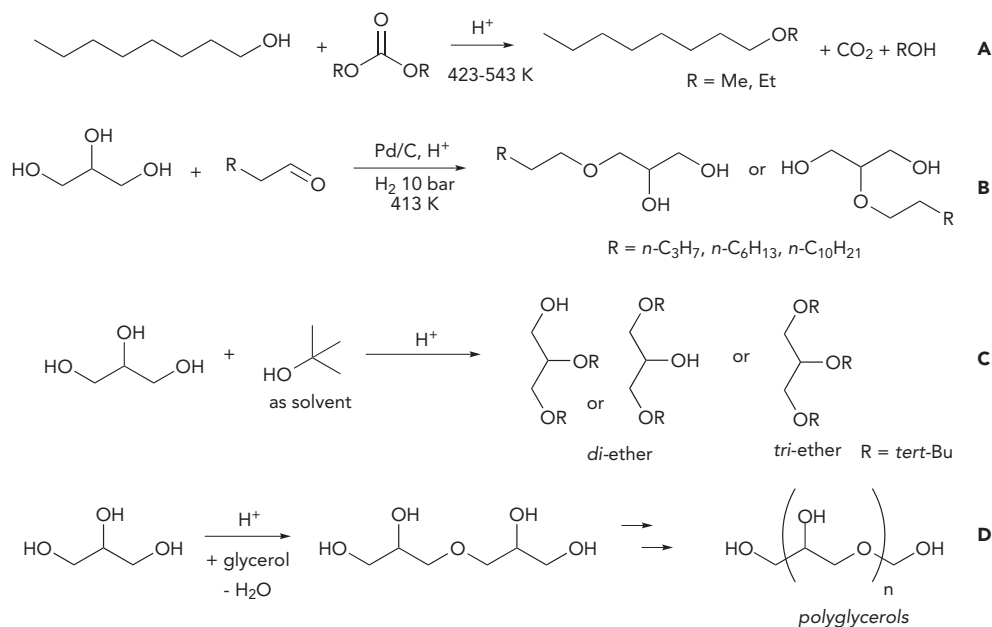
Ethers can be used as fuels or fuel additives, for example, methyl *tert*-butyl ethers were widely used to increase octane numbers, whereas longer chain primary ethers (e.g., di-*n*-pentyl ether and di-*n*-hexyl ether) can enhance diesel fuel cetane numbers (ignition quality, 0.5–5.0 wt % of ether can improve the cetane number by 15%) and reduce carbon monoxide emissions.⁴⁸ In addition, the oligomerization of glycerol plays an important role in the conversion of sustainable sources into surfactants.⁴⁹ The main side reaction in etherification is the dehydration of alcohols to alkenes at higher temperature, and the catalysts that promote etherification are inhibited by water that forms during the reaction.

Alcohol Addition to Alkenes

tert-Butyl ethers hold a prominent role among the oxygenated additives proposed to blend with gasoline. Acid-catalyzed etherification of glycerol with isobutylene (Scheme 5) is a well-studied strategy and is catalyzed by *p*-toluenesulfonic acid, sulfonic acid, and sulfosuccinic acid as well as Amberlyst catalysts.⁵⁰ Higher ethers (diethers and triethers) that form by secondary reactions can boost octane and replace methyl *tert*-butyl ether. Fossil-sourced isobutylene is most commonly used in the reaction, but a renewable route to the feedstock is also feasible. Isobutanol can be produced through carbonylation of propylene or microbial fermentation of sugars,⁷ and glycerol and dehydration of isobutanol over acid catalysts can give the desired isobutylene.

Etherification among Alcohols

The intermolecular condensation reaction of primary alcohols gives primary ethers. Among them, dimethyl ether (DME) is a promising alternative compression ignition fuel. The conversion of longer aliphatic alcohols (C \geq 4) to fuels or additives (especially di-*n*-pentyl ether and di-*n*-hexyl ether) is also of great interest.⁴⁸ Ion-exchanged resin catalysts (e.g., Nafion-H, Amberlyst-15, and Amberlyst-70) and solid acids (e.g., γ -alumina, aluminosilicate zeolites, montmorillonite, and heteropolyacids) are commonly used in the synthesis of aliphatic ethers.

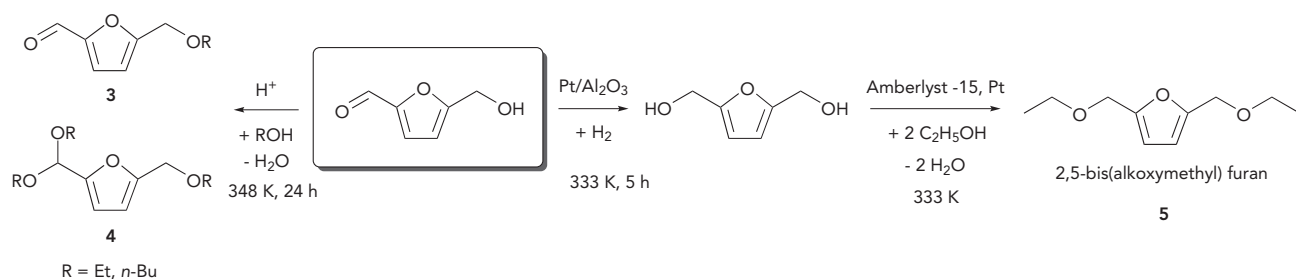


Scheme 6. Pathways to Produce Asymmetric Aliphatic Ethers

- (A) 1-Octanol reacts with carbonate to produce asymmetric ethers.
 (B) Reductive etherification of glycerol with aliphatic aldehydes.
 (C) Etherification of glycerol with *tert*-butyl alcohol.
 (D) Polymerization of glycerol.

Etherification reactions of mixtures of two different alcohols produce self- and cross-condensation products. Carbonates have been used as alkylation reagents to modify the selectivities toward specific products. For example, an 86% yield of 1-methoxyoctane was obtained from methylation of 1-octanol using γ - Al_2O_3 or ion-exchanged resin in the presence of dimethyl carbonate (Scheme 6A).⁵¹ Alternatively, the reductive etherification of carbonyl compounds with alcohols in the presence of hydrogen gas or secondary alcohols as hydride donor can also produce asymmetric ethers. Bethmont et al.⁵² used Pd/C catalysts for the reductive etherification of aldehydes and ketones with alcohols. Yields of asymmetric ethers up to 95% were obtained in the presence of a Brønsted acid co-catalyst under 40 bar H_2 at 373 K. Thus, this system was able to achieve the reductive etherification of aliphatic aldehyde with glycerol to produce 1-*O*-alkyl mono- and diglycerol ethers in one step with yields of 71%–94% and high regioselectivity to the 1-*O*-alkyl monoethers over the 2-*O*-alkyl monoethers (Scheme 6B). Later, Gooßen and Linder⁵³ found that Pt catalysts promoted similar reaction pathways yet enabled the reaction to proceed under mild conditions (323 K, ambient pressure).

The reaction of *tert*-butyl alcohol (TBA) with glycerol produces other promising asymmetric ethers and is appealing because it avoids the need to use a separate solvent (here TBA acts as solvent and reactant). Mono-*tert*-butyl ethers of glycerol are useful as solvent-surfactants; however, they have low solubility in diesel fuel. Moreover, the monoetherification of glycerol with long-chain alcohols is difficult using Brønsted acid catalysts as a result of significant side reactions (e.g., dehydration and self-etherification). Liu et al.⁵⁴ demonstrated that selectivity for monoalkyl glyceryl ether products used in surfactant applications was improved using homogeneous Lewis acids catalysts for the reaction of glycerol with primary alcohols with chain lengths of four to six carbon atoms. Many acid catalysts



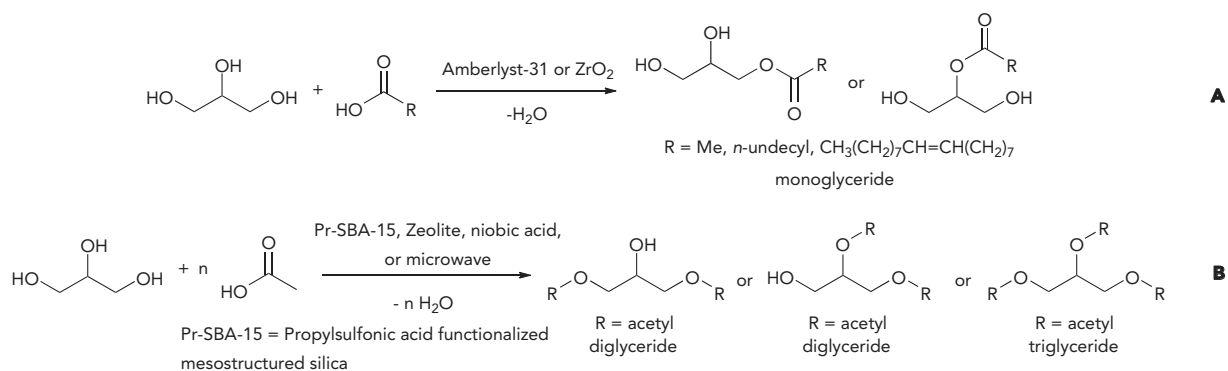
Scheme 7. Etherification of 5-(Hydroxymethyl) Furfural to Fuel Additives

(e.g., SO_3H -functionalized ionic liquids and heterogeneous catalysts such as Amberlyst-15, Nafion, $\gamma\text{-Al}_2\text{O}_3$, and β -zeolite⁵⁵) were tested for their effectiveness in the etherification of glycerol to generate diesel fuels additives: diethers and triethers (Scheme 6C).⁵⁶ Among these catalysts, submicrometer-sized β -zeolite gave the highest conversion of glycerol (95%) and selectivities of 45% and 54% to di-*tert*-butyl and tri-*tert*-butyl ether, respectively.⁵⁵ This is attributed to the presence of mesopores originating from intercrystalline voids that exist in submicrometer-sized-zeolite.

Oligomerization of glycerol produces another class of potentially useful ethers for biosurfactants or hydrotropes (Scheme 6D). Researchers have attempted to produce di- and triglycerols as starting materials for food and cosmetic emulsifiers using acidic resins, zeolites, and sodium carbonate.¹ Early efforts produced di- and triglycerols with combined selectivities up to 65% over Na-zeolites and sodium silicate; however, diglycerol selectivities greater than 90% (80% glycerol conversion, 533 K) were achieved on a basic mesoporous ZSM-5 (Si/Al ratio of 28) impregnated with cesium.⁴⁹ These results led to the use of CsHCO_3 as a homogeneous catalyst for the etherification of glycerol to oligoglycerol and gave 100% linear diglycerol at a low glycerol conversion. Various homogeneous Lewis acids (triflates and triflimidates) were also efficient (up to 80% conversion and greater than 90% selectivity to oligoglycerols) in the oligomerization of glycerol, especially when $\text{Bi}(\text{OTf})_3$ and $\text{Al}(\text{TFSI})_3$ were used.⁵⁷ Alkaline-earth metal oxides (CaO, SrO, BaO, and Mg-Al mixed oxides) also showed high selectivities toward di- and triglycerols (>90%) at 60% conversion.⁵⁸

Etherification of Furans

HMF can be transformed into high-carbon-number ethers, several of which have energy densities comparable with that of gasoline and have been considered as gasoline additives. Generally, solid Brønsted acid catalysts (e.g., sulfonic-acid-functionalized resins, Amberlyst-15, and Dowex DR2030) are effective for such transformations.⁵⁹ The catalyzed etherification reactions produced mixtures of potential bio-diesel candidates such as 5-(alkoxymethyl) furfural (3) and dialkyl acetal, whereas 2,5-bis(alkoxymethyl) furan (5), a potential diesel additive, was produced by sequential reduction and etherification reactions catalyzed by Pt or Pt/Sn supported on Al_2O_3 and Amberlyst-15, respectively (Scheme 7). In such reactions, the 2,5-substituted hydroxyl and formyl groups are highly reactive and easily form polymers such as humins that block pores. Moreover, ring-opening reactions of the furans and formation of acetals lead to yield losses. Thus, the development of more robust and selective catalysts has been a primary focus of work in this area. These problems are partially resolved by using mesoporous acid catalysts. For example, Lanzafame et al.⁶⁰ used mesoporous acid catalysts (e.g., Al-MCM-41



Scheme 8. Acid-Catalyzed Esterification of Glycerol

(A) Esterification of glycerol to monoglyceride.

(B) Acetylation of glycerol to diacetyl and triacetyl glycerol.

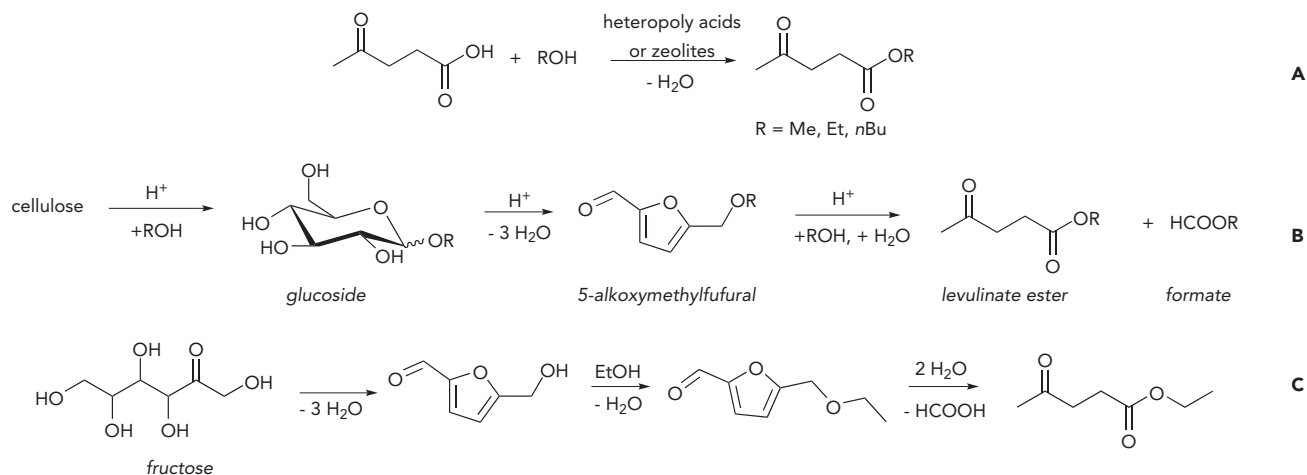
and SBA-15-supported sulfated zirconia) to convert HMF to 5-(ethoxymethyl) furan-2-carbaldehyde (5EMF) with yields up to 76%.

Esterification

Triglycerides obtained from plant oil and animal fat are abundant natural esters; however, their use as biofuels or additives is limited because their carbon numbers are not in the appropriate range. This mismatch has motivated investigations into the further conversion of triglycerides and their derivatives. Monoglycerides are used in the production of detergents and packaged food; however, the traditional methods used to produce monoglycerides (homogeneous acid catalysis with sulfuric or *p*-toluenesulfonic acid) give low selectivities and introduce corrosion problems. Pouilloux et al.⁶¹ found that reaction of glycerol with fatty acids over Amberlyst-31 gave 90% yield and 85% selectivity to the monoglyceride at 363 K (Scheme 8A). Zirconia-based solid acids (e.g., ZrO_2 , $\text{TiO}_2\text{-ZrO}_2$, $\text{WO}_x/\text{TiO}_2\text{-ZrO}_2$, and $\text{MoO}_x/\text{TiO}_2\text{-ZrO}_2$) also catalyzed acetylation of glycerol with high conversions and selectivities (e.g., $\text{MoO}_x/\text{TiO}_2\text{-ZrO}_2$ achieved nearly 100% glycerol conversion). Within these systems, monoglycerides are the predominant product over di- and triglycerides, even at acetic acid to glycerol ratios of 6:1 (Scheme 8A).⁶²

Compared with monoglycerides, diacetyl glycerol (DAG) and triacetyl glycerol (TAG) are superior fuel additives and improve cold flow and viscosity properties or anti-knocking properties when blended with gasoline. Sulfuric- and molybdophosphoric-acid-functionalized SBA-15 materials produce these acetylated derivatives (DAG and TAG) by esterification of glycerol with acetic acid with excellent conversion (90%) and selectivity (>85%) at 398 K with an 9:1 acetic acid to glycerol ratio (Scheme 8B).⁶³ Gonçalves et al.⁶⁴ later studied a series of acid catalysts that showed reactivities decreased in the order Amberlyst-15 > K-10 montmorillonite > niobic acid > H-ZSM-5 zeolite.

Acetyl glycerol can also be produced using methyl acetate as the acetyl source. Arene-sulfonic-acid-functionalized mesostructured silicas and Amberlyst-70 and Nafion-SAC-13 can catalyze the transesterification of glycerol with methyl acetate to di- and triacetyl glycerols as the main products (74%) with 99.5% glycerol conversion at 443 K, although high methyl acetate to glycerol ratios (50:1) are required.⁶⁵ In contrast, acetic anhydride can be used as an acylation reagent at nearly



Scheme 9. Production of Levulinic Esters

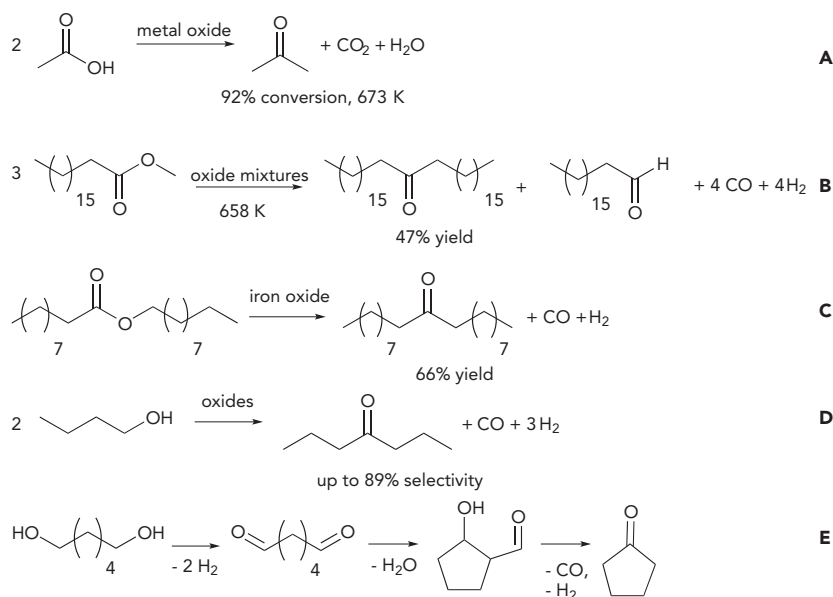
- (A) Esterification of levulinic acids with alcohols.
 (B) Direct conversion of cellulose to levulinic esters.
 (C) Conversion of fructose to ethyl levulinate.

stoichiometric feed ratio (4:1 acetic anhydride to glycerol) and at lower temperatures. Reactions of acetic anhydride with glycerol achieved 100% selectivity to triacetyl glycerol and complete glycerol conversion within 20 min at 333 K over β -zeolite and K-10 montmorillonite. Control experiments showed that reactions of glycerol with acetic acid as the acylation reagent gave much lower selectivity to triacetyl glycerol under similar conditions.⁶⁶

The transesterification of triglyceride vegetable oils with short-chain alcohols (methanol and ethanol) to alkyl esters for the production of bio-diesel is straightforward and effective. Direct esterification of carboxylic acids (e.g., fatty acid from soybean and rapeseed oil or LA from cellulose hydrolysis) with alcohols is also useful because it assists in the pre-treatment of these feedstocks before the production of bio-diesel and other products. To this end, Nafion/silica composites and organo-sulfonic-acid-functionalized mesoporous silicas effectively catalyze direct esterification of fatty acids with methanol.⁶⁷

Alkyl levulinates, especially ethyl and *n*-butyl levulinate, are excellent octane boosters for gasoline and fuel extenders for diesel. These species can be produced by esterification of LA with alcohols over heteropoly acid and zeolite catalysts, among others (Scheme 9A). Interestingly, a bio-catalytic pathway to alkyl levulinates using immobilized *Candida antarctica* lipase B (Novozym 435) on a macroporous polyacrylic resin was reported.⁶⁸

Finally, levulinic esters can be produced from cellulosic residue more directly using an acid-catalyzed reaction with alcohols (Scheme 9B).⁶⁹ Sulfated metal oxides (e.g., $\text{SO}_2^{4-}/\text{TiO}_2$) convert sugars into methyl levulinate in methanol at moderate temperatures (473 K, 2 hr) with high yields from sucrose (43%), glucose (33%), and fructose (59%). The resulting liquids include alkyl levulinate, dialkyl ethers, and alcohol, which can be easily separated by fractionation. The highest yields were achieved with fructose, which involves the conversion of furfuryl alcohol into alkyl levulinate catalyzed by a solid acid catalyst, such as ion-exchanged resins, zeolites, sulfonic-acid-functionalized SBA-15, or ionic liquids (Scheme 9C).



Scheme 10. Ketonization of Different Starting Materials

- (A) Ketonization of acetic acid to produce acetone.
 (B) Ketonization of methyl ester to ketone.
 (C) Ketonization of symmetrical ester to ketone.
 (D) Ketonization of alcohol to ketone.
 (E) 1,6-Hexanediol ketonization to cyclopentanone.

Ketonization

Ketonization is an efficient way to produce ketones and was industrialized in the 1920s. Homogeneous catalysts such as carbonates (e.g., CaCO_3 and BaCO_3) ketonize acetic acid to acetone via the acetate intermediate. The ketonization of acetic acid to acetone on heterogeneous chromia catalysts in a fixed-bed flow system was reported in 1969, and the proposed bimolecular mechanism involves the reaction between surface stabilized acetate and acylcarbonium ions to give acetone, carbon dioxide, and water.⁷⁰ The carbon dioxide and water produced during ketonization reactions inhibit the acid and base functions of most ketonization catalysts and significantly reduce yields.

Metal oxide (MgO , CaO , BaO , and ZnO) particles supported on high surface area silica or activated carbon are effective catalysts for the production of acetone from acetic acid (e.g., 78% yield on MgO). However, water suppresses reaction rates, perhaps because it hydrolyzes the acetate intermediate or forms less active hydroxide particles (Scheme 10A).⁷¹ Similarly, increased concentration of carbon dioxide and water were shown to significantly reduce the yield of ketonization products on $\text{CeO}_2/\text{ZrO}_2$ catalysts as well. $\text{CeO}_2/\text{Al}_2\text{O}_3$ catalysts were also seen to be promising for the reaction and capable of producing several long-chain ketones such as 3-pentanone, 6-undecanone, and 7-tridecanone.⁷²

In addition to the carboxylic acids, the methyl esters of such acids can also undergo ketonization reactions. For example, methyl esters obtained by transesterification of erucic acid present in rapeseed oil can be ketonized using a complex mixture of metal oxides ($\text{Sn}/\text{Ce}/\text{Rh}$ ratios of 90:9:1, Scheme 10B).⁷³ Similar chemistry is catalyzed by iron-oxide-based particles that convert the symmetrical *n*-decyl *n*-decylate ester to the corresponding ketone with 66% yield (Scheme 10C).

Primary alcohols (e.g., 1-butanol) undergo ketonization on iron oxide, chromia, and mixed Sn–Ce–Rh oxides (Scheme 10D). Dipropyl ketone was obtained with 89% selectivity at 88% 1-butanol conversion using Sn–Ce–Rh oxide at 623 K.⁷⁴ At lower temperatures, *n*-butyraldehyde was the main product, demonstrating the dehydrogenation ability of the catalyst. This observation, along with the conversion of butyl butyrate on the catalysts suggested that ketones may form by the Tishchenko reaction of the aldehydes to form esters and the subsequent conversion of the esters to ketone.⁷⁴ Ketonization of carboxylic acids gives linear compounds, and such compounds are desirable as blend stocks for diesel after hydrodeoxygenation of the ketone moiety. On the other hand, diacids allow for the formation of cyclic ketones. For example, adipic acid, which can be sourced through microbial fermentation of sugars, gives cyclopentanone on ketonization.⁷⁵ Cyclopentanone may also be obtained from 1,6-hexanediol (Scheme 10E). This reaction has been demonstrated over CeO₂–MnO_x and involves aldol condensation of the aldehyde obtained from the diol, followed by elimination of the primary carbonyl group. The cyclopentanone so obtained is an important intermediate and can be used for producing jet fuels via aldol-type condensation reactions.⁷⁶

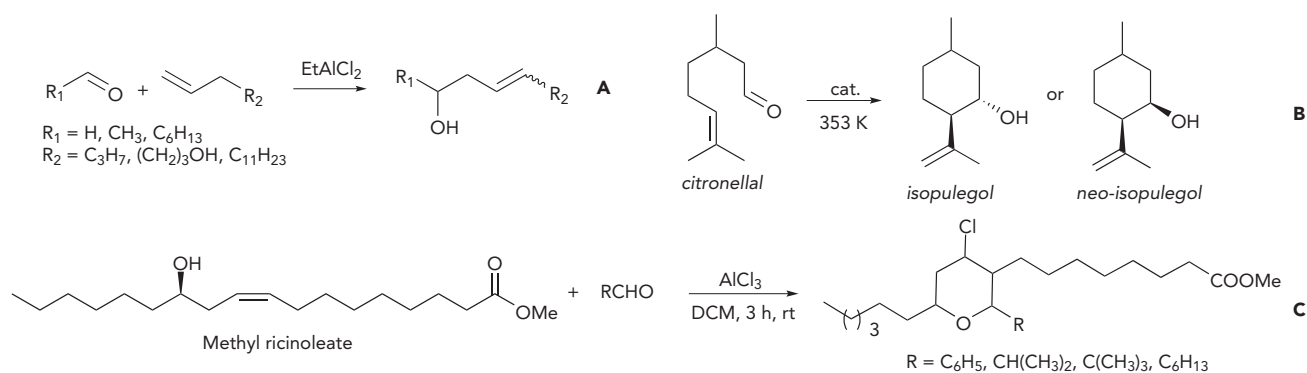
PROMISING AND EMERGING TRANSFORMATIONS

In addition to the reactions described above, a number of other reactions provide unique opportunities to upgrade bio-derived platform chemicals to more valuable products. These reactions are well known within the organic chemistry community; however, they are receiving attention only recently for catalytic upgrading of biomass. New findings show that these reactions can fill specific gaps in the portfolio of oxygenated conversions and, thus, provide unique pathways to produce higher value chemicals from biomass-derived building blocks. We speculate that recent work on mechanistic studies and catalyst design, coupled with the growing availability of feedstocks, will increase the appeal and practicality of the following sets of chemistry.

Prins Reaction

The Prins reaction is the acid-catalyzed electrophilic addition of an aldehyde or ketone to an alkene or alkyne, which can produce diols or esters if nucleophilic species (e.g., water or acids) are present in the solvent. For example, Snider and Phillips⁷⁷ reported the production of long-chain unsaturated diols (e.g., hept-3-ene-1,7-diol from reaction of 5-hexen-1-ol with formaldehyde, 59% yield) using a stoichiometric amount of EtAlCl₂ as the catalyst. Such diols may be oligomerized to produce larger ethers and may be used subsequently as fuel additives or as comonomers in the production of polyesters and polyurethanes. The Prins reaction can also produce homoallylic alcohols from reactions of carbonyl compounds with alkenes. The reaction of acetaldehyde or heptanal as carbonyl compounds generated moderate yields even in short reaction times (6 min) at 273 K using EtAlCl₂ (Scheme 11A).⁷⁷

Prins chemistry offers a route for converting 1-butanol, for example, into oct-6-en-4-ol or oct-6-en-4-one by converting the 1-butanol into 1-butene and butyraldehyde and then coupling these intermediates by the Prins reaction. In contrast, the Guerbet reaction produces only 2-EH, a branched alcohol, from reactions of 1-butanol. Thus, a scheme of reactions involving the Prins and Guerbet reactions at different stages may provide an elegant method to manipulate the degree of branching among the products. In turn, this could allow for engineering processes with better control on several properties such as octane number, cetane number, and pour point for



Scheme 11. Prins Reaction of Aldehydes with Differently Functionalized Alkenes

(A) Prins reaction of aldehydes with aliphatic alkenes.

(B) Intermolecular Prins reaction of citronellal.

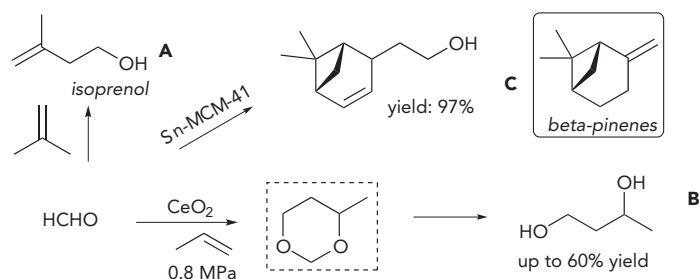
(C) Prins reaction of methyl ricinoleate with aldehydes.

fuels, viscosity of lubricants, reactivity of intermediates, or crystallinity, and glass transition temperature in potentially novel polymers.

Isopulegols, intermediates used to produce fragrances, can be produced with yields greater than 95% by intramolecular Prins cyclization of citronellal over mesoporous materials containing aluminum and zirconium (Scheme 11B). The Prins condensation of methyl ricinoleate, obtained by transesterification of castor oil with aldehydes gave 2,3,6-trialkyl-substituted 4-chlorotetrahydropyrans in good yields (70%–76%) over an $AlCl_3$ catalyst (Scheme 11C). The chlorine atom in the product, generated by intercepting the Prins intermediate with a chloride from the catalyst,⁷⁸ can be removed by hydrodechlorination using heterogeneous palladium catalysts. Subsequent hydrogenation of the tetrahydro-2H-pyran ring can produce longer hydrocarbons with alkyl side chains of different lengths.

The Prins reaction has been used to produce isoprenol, which is an important synthesis block for industrially valuable terpenes, by the reaction of isobutylene and formaldehyde over Lewis acid catalysts such as $SnCl_4$ and $ZnCl_2$. The same reaction was also catalyzed by $SnCl_4$ anchored on MCM-41 by a quaternary ammonium chloride linker, which gave a 90% yield of isoprenol after 3.5 hr at 333 K (Scheme 12A).⁷⁹ Wang et al.⁸⁰ demonstrated the synthesis of 1,3-butanediol, a co-monomer in polyurethane and polyester resin, from the one-pot reaction of formaldehyde with propylene over ceria. The Prins reaction initially produces a 1,3-dioxane intermediate that is readily hydrolyzed to form 1,3-butanediol. This simple reaction provides a 60% yield of 1,3-butanediol using a ceria catalyst made by a simple precipitation method (Scheme 12B).

α - and β -Pinenes are the major terpene components of wood turpentine and of numerous other volatile oils. The reaction of β -pinene with formaldehyde has been known since the early 1940s. The product, nopol, an optically active bicyclic primary alcohol, has been used in the agrochemical industry to produce pesticides, soap, and perfume. Apart from the use of homogeneous zinc chloride and acetic acid as catalysts, this reaction was recently revisited by chemists using heterogeneous catalysts. In 2002, Villa de P et al.⁸¹ reported the synthesis of Sn-grafted MCM-41 catalysts for this reaction with yields as high as 97%, and more interestingly, the activity increased after several runs (Scheme 12C). Other catalysts (e.g., Fe–Zn double metal cyanide complexes, sulfated zirconia, Zr-SBA-15, sulfated zinc ferrite,



Scheme 12. Prins Reaction of Alkenes with Formaldehyde

(A) Prins reaction with isobutylene to produce isoprenol.

(B) Direct synthesis of 1,3-butanediol via Prins reaction with propylene.

(C) Prins reaction with β-pinenes.

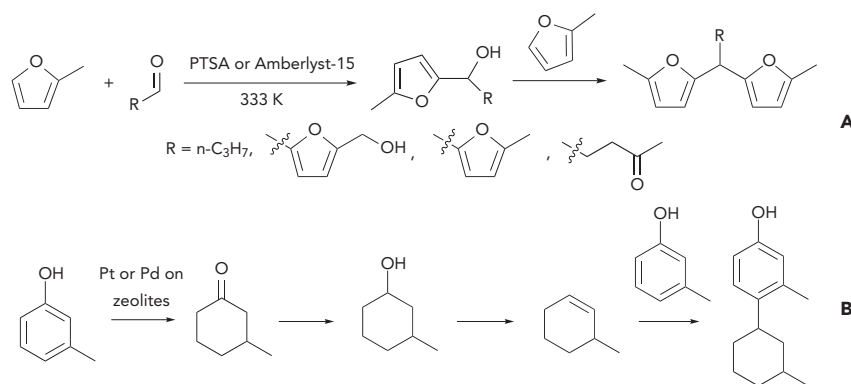
and ZnCl₂-impregnated montmorillonite) were also active for this transformation. Notably, Zn/Cr mixed metal oxide, with an optimum Zn/Cr atomic ratio of 1:6, gave 100% selectivity to nopol at 97% β-pinene conversion.⁸²

Hydroalkylation and Alkylation

Hydroalkylation reactions can increase the carbon number of furans and phenols and are an appealing alternative to simple hydrodeoxygenation of these mid-sized reactants. In 2011, Corma et al.⁸³ reported that *para*-toluenesulfonic acid and Amberlyst-15 catalyzed the reaction of two molecules of 2-methylfuran with one aldehyde to form bisalkylalkane, which after further treatment gave alkanes suitable for biodiesel. Apart from butyraldehyde, HMF and 5-methylfurfural derived from hexoses were also suitable reactants for this transformation and gave up to 93% conversion and 95% selectivity (Scheme 13A). More interestingly, the trimerization of 2-methylfuran was also realized through the in situ formation of 4-oxopentanal from the ring opening of one equivalent of 2-methylfuran with water.⁸³ The same authors later reported detailed studies on the reaction of 5-methylfurfural with 2-methylfuran and found other solid acid catalysts (e.g., β-zeolite and USY zeolite) to be active for alkylating furanics with C₂–C₅ *n*-aldehydes.⁸⁴

Corma et al.⁸⁴ later extended these studies to include ketones as alkylating agents and found that acetone and 2-pentanone gave products similar to those seen with aldehydes, albeit with somewhat lower conversion and selectivities. Work by Zhao et al.⁸⁵ illustrated that a combination of hydrogen transfer and acid-catalyzed alkylation reaction produced bicyclohexanes from reactions of phenol and substituted phenols over a number of solid Brønsted acid catalysts including Amberlyst-15, sulfated zirconia, heteropolyacids, and zeolites. Importantly, H-β-zeolites gave high yields of polycyclic alkylation products even within liquid water, whereas meso- and macroporous solid acids showed little reactivity. Anaya et al.⁸⁶ demonstrated that hydroalkylation of *m*-cresol over Pt- and Pd-containing zeolites (H-Y and H-MOR) gave a distribution of products containing two or more six-carbon rings (e.g., dimethyl bicyclohexanes) (Scheme 13B). Yields for the alkylation products and the related intermediates, including methylcyclohexanone, approached 80% after the ratio of the metal to acid sites was tuned to optimize the rates of hydrogen transfer, dehydration, and alkylation steps. Overall, such alkylation reactions of substituted furanics and phenolics, obtained from pyrolysis of lignin, can produce polycyclic hydrocarbons (e.g., C₁₄₊) that may be ring opened and used as fuels.

Recent and promising work shows that transalkylation reactions of 2,5-dimethylfuran (from glucose isomerization and dehydration) with ethylene (obtained from ethanol



Scheme 13. Examples of Hydroalkylation and Alkylation Reactions

(A) Hydroalkylation of 2-methylfuran with aldehydes.

(B) Self-alkylation among *m*-cresol-derived species.

dehydration) followed by isomerization can produce paraxylene with selectivities of 75% and 90% at acid sites within H-Y and H- β -zeolites, respectively.⁸⁷ This chemistry provides a renewable pathway from sugars to the production of building-block aromatics, which are critical for the production of polyesters, among other polymers, and have higher value than precursors to fuels.

Benzoïn Condensation

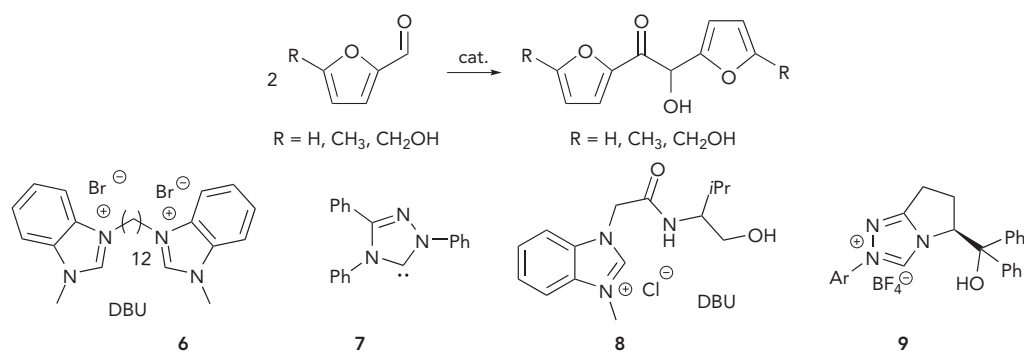
The benzoïn condensation is the reaction between two aldehydes and can be catalyzed by nucleophiles, such as cyanide anion or N-heterocyclic carbene (NHC). The reaction takes place by the addition of the cyanide anion or NHC to the aldehydes and proton transfer to form an acyl anion equivalent that adds to the second aldehyde. The benzoïn condensation reaction of furfural was reported first by Stetter and further exploited by Lee et al.⁸⁸ In 2008, a fuoin yield of 86% was obtained only after a reaction for 1.5 hr catalyzed by methylene-bridged bis(benzimidazolium) salt (**6**) in water at room temperature (Scheme 14).⁸⁹

Later, HMF was converted to 5,5'-di(hydroxymethyl)fuoin (DHMF), a promising C₁₂ intermediate for kerosene and jet fuel, with 98% yield catalyzed by the ionic liquid 1-ethyl-3-methylimidazolium acetate in the presence of DBU.⁹⁰ In addition, the NHC catalyst (**7**) and (**8**) effectively converted HMF, MF, and furfural to the corresponding fuoin derivatives. An asymmetric variant of the benzoïn condensation of furfural was achieved using triazolium salt (**9**) as a catalyst, which gave moderate to good enantioselectivity (64%–88% ee) at temperatures below 273 K.⁹¹

Diels-Alder Reaction

The Diels-Alder (DA) reaction is the cycloaddition reaction between a conjugated diene and a substituted alkene to form a substituted cyclohexene. DA reactions can proceed without catalysts, but the rates are greatly increased by Lewis acids. The thermodynamics of DA reactions that utilize furans as the diene are generally unfavorable because the aromatic character of the furan is broken and strain is generated in the resulting bicyclo[2.2.1]heptane. Thus, high pressure is normally required for the DA reaction with furan. Early in 1976, Dauben and Krabbenhoft⁹² found that high pressure can enhance the yields of products in the reaction of furans with a series of dienophiles (Scheme 15A).

The DA approach was applied to the reaction of 2,5-dimethylfuran (DMF) with acrolein to produce 7-oxabicyclo[2,2,1]hept-2-ene, which after further transformation,



Scheme 14. Benzoin Condensation of Furfural

can produce polyethylene terephthalate (PET). In this reaction, the DMF can be generated from the hydrogenation of HMF, and acrolein can be prepared from the dehydration of glycerol (Scheme 15A).⁹³

The DA reaction of alkali-conjugated and elaidinized safflower fatty acids with acrylic, methacrylic, crotonic, and cinnamic acids and their esters was achieved with 40%–64% yields at 373–483 K. aus dem Kahmen and Schäfer⁹⁴ found that methyl conjugate reacted readily with different dienophiles in 55%–90% yields (Scheme 15B). The reaction was accelerated in the presence of 1–1.8 equivalents of Lewis acids such as BCl_3 , $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, or catalytic amounts of iodine. In addition, methyl *E*-12-oxo-10-octadecenoate was reacted with the dienes 2-(trimethylsilyloxy)-1,3-butadiene and 2,3-dimethylbutadiene to produce the cycloadducts in 69% and 86% yield, respectively (Scheme 15C).⁹⁴

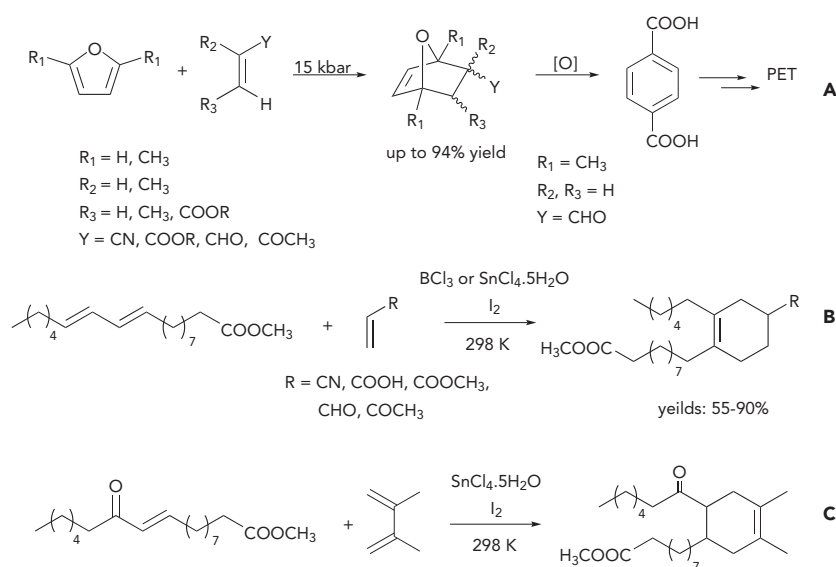
CONDENSATION PROCESSES AS SIDE REACTIONS

The reactions discussed above provide effective and powerful strategies to produce high-value fuels, fuel additives, and other useful chemicals. However, undesired condensation reactions can be problematic during many upgrading processes. For example, condensation of lignin can take place between the benzylic cations and the electron-rich aromatic carbon on aromatic rings of lignin (Scheme 16A) during acid-catalyzed depolymerization or coupling reactions.⁹⁵ In addition, the formation of humins (dark, recalcitrant solids) is inevitable during the acid-catalyzed production of LA from HMF. Detailed work by Patil and Lund⁹⁶ showed that humins form via a 2,5-dioxo-6-hydroxy-hexanal intermediate and subsequent aldol condensation at either the 3, 4, or 6 carbon with the carbonyl group on the HMF (Scheme 16B). Etherification, esterification, and acetalization may all occur as undesirable side reactions at many of the conditions described in this review because all these chemistries are promoted by acid catalysts.

FROM CONDENSATION PRODUCTS TO FUELS OR ADDITIVES

Hydrodeoxygenation and Hydrogenolysis

Some products from condensation reactions, such as ethers and solketal, can be used directly as fuel additives. On the other hand, other oxygenates, such as ketones from ketonization and aldol condensations, require further transformations to obtain hydrocarbon biofuels or additives. Here, either coupled dehydration and hydrogen transfer or hydrogenolysis steps are critical pathways to remove oxygen from products formed via the condensation reactions described above. For example, tricosane may be obtained from two molecules of lauric acid by ketonization on MgO and



Scheme 15. DA reaction of Chemicals from Biomass

(A) DA reaction of furans with different dienophiles.

(B) DA reaction of methyl conjugate.

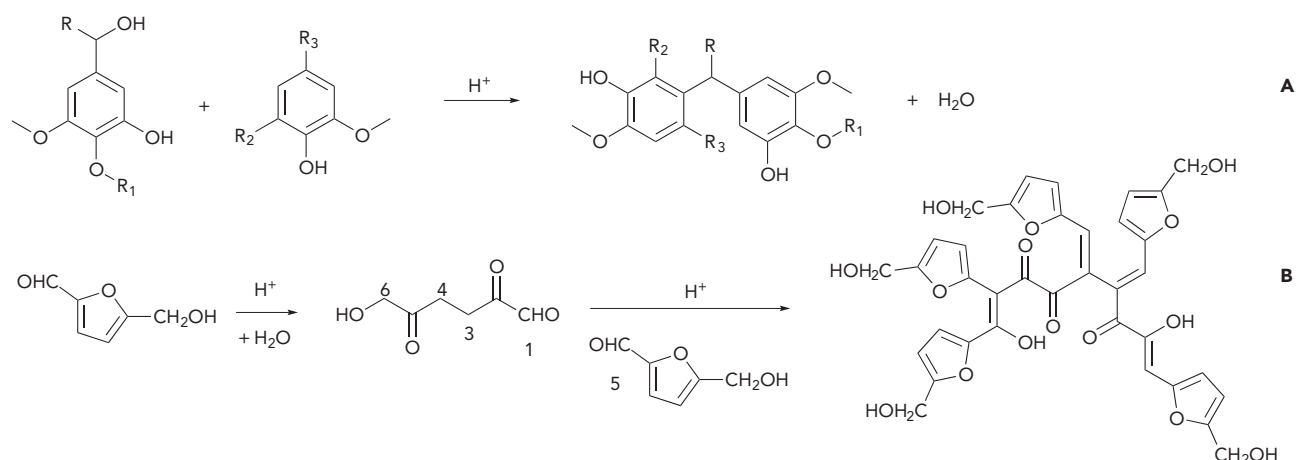
(C) DA reaction of methyl *E*-12-oxo-10-octadecenoate with 2,3-dimethylbutadiene.

subsequent dehydration and hydrogenation reactions catalyzed by Pt-MgO or Pt-Al₂O₃.⁹⁷ Similarly, the products from aldol condensation of acetone with furfural or HMF (C₇–C₁₅ oxygenates) were reduced to liquid alkanes by hydrogenation with Pd/Al₂O₃ to (10) and subsequent dehydration and hydrogenation over bifunctional Pt/SiO₂-Al₂O₃ catalysts (Scheme 17A).³⁵ Hydrodeoxygenation (HDO) over metal nanocluster catalysts (e.g., Pt, Ru, and Ir) progresses via hydrogenolysis reactions at elevated temperatures and high hydrogen pressures. On the other hand, bifunctional catalysts containing metal and acid sites such as Pt-containing zeolites or Rh-Re⁹⁸ bimetallic clusters, are known to catalyze the reaction even under milder conditions. Rh-Re can catalyze the selective cleavage of secondary C–O bonds within cyclic ethers and polyols to produce α,ω -diols from furfuryl alcohol and 2-(hydroxymethyl)tetrahydropyran in water with selectivities exceeding 97% at 393 K.⁹⁸

Furoins (e.g., 5,5'-dihydroxymethyl furoin) resulting from the condensation of furfural products are water soluble and amenable to aqueous hydrodeoxygenation, as was shown with a [Pt/C + TaOPO₄] catalyst, which produced alkanes with 96% selectivity containing 46% *n*-dodecane (Scheme 17B).⁹⁹ Such methods normally require harsh reaction conditions to ring open tetrahydrofuran and remove oxygen. Sutton et al.¹⁰⁰ proposed an alternative method to produce alkanes by hydrolytic ring opening of intermediate furans to form polyketones. The polyketones were then converted into linear alkanes in the presence of La(OTf)₃ and Pd/C catalysts in acetic acid after 12–16 hr at 473 K (Scheme 17C). A similar system was also reported for the conversion of DHMF into liquid hydrocarbon fuel (78% alkanes).

SUMMARY AND OUTLOOK

In order to resolve the issues of the increasing pressure on resources from the growing world population, the ever-increasing demand for high-value chemicals, and the threat of climate change, it is imperative that we begin to use bio-derived alternatives to existing fuels and chemicals. Chemistry and catalysis will be the

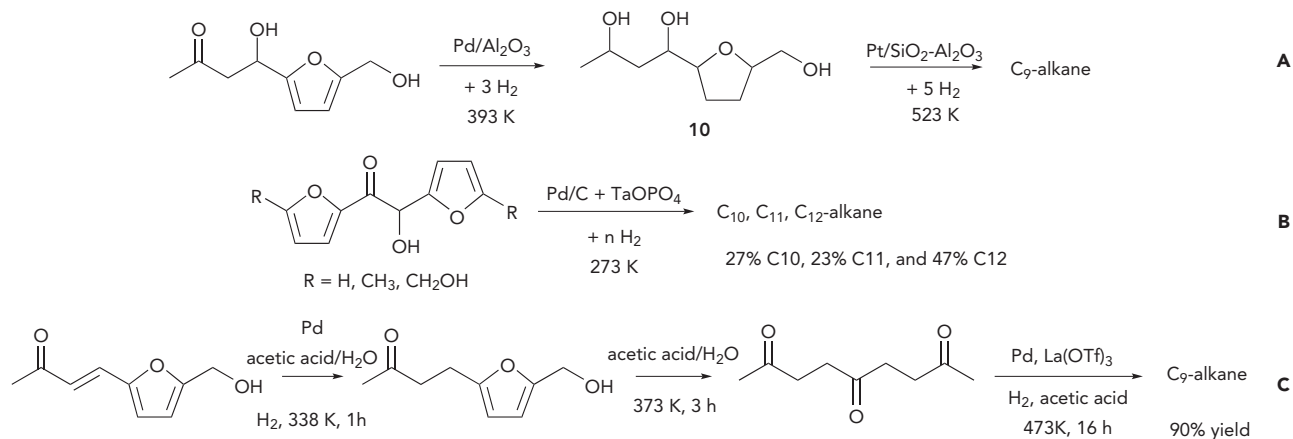


Scheme 16. Undesirable Condensation Reactions that Form Recalcitrant Residues during Biomass Conversion

(A) Condensation of lignin.

(B) Humins formation via Aldol condensation reaction.

cornerstones of any strategy to realize this objective. In particular, several condensation reactions such as aldol condensation, acetalization, etherification, and esterification can be used to upgrade biomaterials to larger functionalized oxygenates (Scheme 18). These condensation products may have direct applications as detergents and fuel additives or could be hydrodeoxygenated to produce hydrocarbon fuels and lubricants. Many ion-exchanged resins, zeolites, metal oxides (acidic and basic), and homogeneous organic and organometallic complexes can catalyze these transformations; however, improved catalysts and processes are still needed. For example, in the Guerbet reaction of ethanol to 1-butanol, both ethanol conversion rates and 1-butanol selectivities need to be improved if this chemistry is to be practiced. Apart from traditional inorganic catalysts, organocatalysts (e.g., NHCs and ionic liquids) are also emerging as powerful catalysts in laboratory experiments; however, their transfer to larger-scale processes will require significant

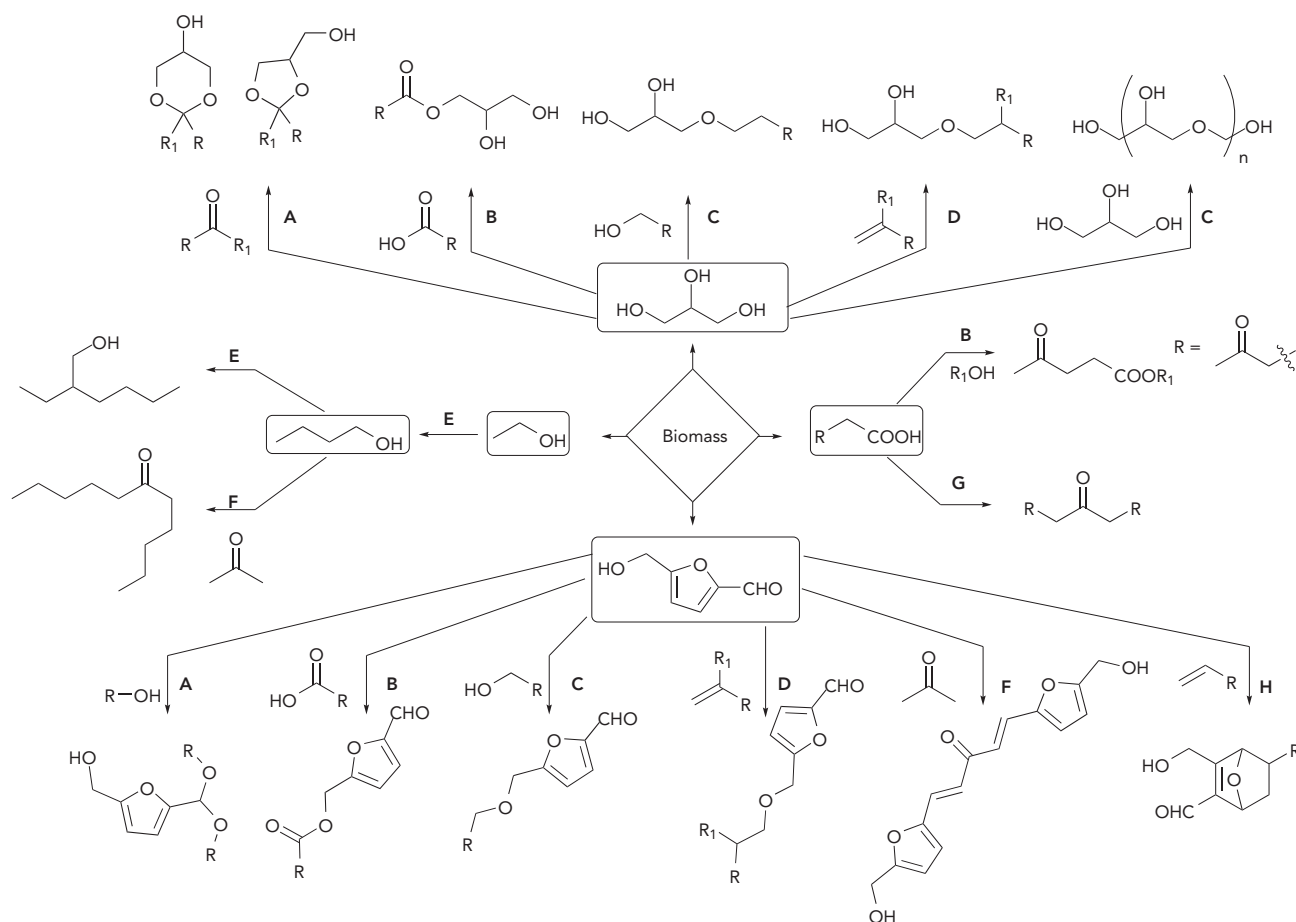


Scheme 17. Hydrogenation and Dehydration/Hydrogenation of Aldol Adducts to Alkane

(A) Stepwise hydrogenation dehydration/hydrogenation of Aldol adducts.

(B) One-pot hydrogenation dehydration/hydrogenation of furfuroins to alkanes.

(C) Hydrolytic ring opening of furans pathway to produce alkenes.



Scheme 18. Condensation Reactions for Upgrading Biomass-Derived Oxygenates into Higher-Value Functionalized Chemicals

- (A) Acetalization.
 (B) Esterification.
 (C) Etherification of alcohols with alcohols.
 (D) Etherification addition of alcohols to alkenes.
 (E) Guerbet reaction.
 (F) Aldol condensation.
 (G) Ketonization.
 (H) Diels-Alder reaction.

developments to improve the recyclability of the catalysts and to achieve process integration. Therefore, process development together with catalyst development will continue to be an important research area. Particularly promising are systems that utilize tandem reactions to produce and use unstable or not easily separated intermediates; these one-pot systems avoid costly processing steps. Given their high reactivity, aldehydes and ketones are relatively difficult to source from biomass, therefore successful schemes may be those in which bio-alcohols are dehydrogenated in situ or reacted with aldehydes and ketones that are derived from petrochemical routes. This might be realized using catalysts with multiple active sites (e.g., combinations of redox, metal, and acid-base sites) or by tuning the distribution of active sites on catalysts by incorporating dopant metals into complex oxides. Ultimately, the road to creating a sustainable renewable industry must involve cooperative efforts between the petrochemical fossil industry, emerging biomass conversion companies, and university research groups to identify conversion chemistries

and processes that can use existing infrastructure to upgrade highly oxygenated biomass species. Through such cooperation, processes may be developed to create value-added compounds with the intent to produce all reagents directly from renewable sources.

AUTHOR CONTRIBUTIONS

L.W., A.A.G., and F.D.T. conceived and coordinated the review. L.W., T.M., A.A.G., and D.W.F. wrote the original manuscript and created the figures. All authors read, revised, and approved the manuscript. D.W.F. and F.D.T. served as principal investigators.

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