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Project Title: Catalytic Upgrading of Key Biorefining Building Blocks to Renewable Chemicals, Polymeric Materials, and Liquid Fuels
Grant Number: DE-FG02-10ER16193
Grant Period: 09/15/13 – 09/14/16; NCE to 07/31/17
Yearly Budget: $150,000
Project PI: Eugene Chen, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872. Telephone: (970) 491-5609. Email: eugene.chen@colostate.edu

Project Abstract

Overall Goal. The central objective of this project is to develop efficient, selective, and cost-effective catalytic systems for upgrading of key biorefining building blocks derived from catalytic conversion of plant biomass into value-added chemicals, polymeric materials, and liquid fuels. More specifically, the proposed work for the current grant period seeks to accomplish the following three specific objectives: (a) developing cost-effective and recyclable catalysts for selective upgrading (direct coupling) of the C_6 biorefining building block 5-hydroxymethylfurfural (HMF) into C_{12} intermediates and for integrating biomass conversion and upgrading processes; (b) transforming the upgraded C_{12} intermediates into polyols, polyurethanes, polyesters, and diesel fuels; and (c) reforming the upgraded intermediates into premium C_{12} centered liquid hydrocarbon transportation fuels via selective hydrodeoxygenation catalysis.

Scientific Methods. The hypothesis-driven research described in the proposal employs combined experimental techniques for mechanistic, structural, and synthetic studies of catalysis as well as for polymer and materials science. Building upon a key discovery that HMF, an established biorefining building block or biomass platform chemical, can be selectively and quantitatively upgraded into the C_{12} 5,5'-di(hydroxymethyl)furoin (DHMF) in a catalytic and 100% atom-economical fashion, the research proposed for the current grant period focuses on selective upgrading of HMF and two other related C_5 and C_6 biorefining building blocks into higher-energy-density C_{10} and C_{12} furoin intermediates and subsequent catalytic reforming of such intermediates into value-added chemicals, polymeric materials, and liquid fuels.

Potential Impacts. The research described in the proposal addresses one of the DOE-BES's priority research directions in Catalysis for Energy, particularly in terms of exploring new catalytic pathways for lignocellulosic biomass conversion and upgrading into chemicals and fuels. Successful outcomes of this project are a new, highly effective DHMF route for plant biomass utilization and catalytic upgrading into chemicals, materials, and fuels, as well as a fundamental understanding of this new approach. Hence, this research would positively impact 3*E*'s: *E*nergy, as it studies nonfood biomass conversion and upgrading into sustainable energy sources or products; *E*conomy, as it concerns chemical catalysis and biomass energy systems, areas central to the global economy; and *E*nvironment, as it utilizes catalytic processes and renewable feedstocks as well as recyclable metal and benign organic catalysts.

Summary Accomplishments

Upgrading of HMF involving C–C bond forming reactions is a necessary step for producing chain-extended intermediates leading to higher-energy-density, higher-quality transportation fuels. However, HMF upgrading through the desired self-condensation coupling was hampered by the fact that it cannot undergo self-aldol condensation due to its lack of α-hydrogen and that it carries the active hydroxyl group, commonly perceived a poison to catalysts employed for the benzoin condensation. Hence, cross-aldol condensation of HMF with enolizable compounds such as acetone was developed as a useful alternative method, but such a method utilizes other organics and also produces small molecules as waste. To address these two issues, we have developed a new greener condensation technology that uses an organic *N*-heterocyclic carbene (NHC) catalyst to reverse the polarity of the HMF carbonyl (umpolung), enabling a solvent-free direct condensation coupling of HMF into DHMF with quantitative yield and 100% atom-economy. The C_{12} DHMF is considered a new bio-derived building block or platform chemical that has been catalytically transformed into renewable fine chemicals, polymeric materials, and oxygenated biodiesel or premium alkane jet fuels (Fig. 1). This umpolung condensation-coupling route is the key part of the "Green Condensation Reactions for Renewable Chemicals, Liquid Fuels, and Biodegradable Polymers" technology that won the ***2015 Presidential Green Chemistry Challenge Award*** sponsored by EPA in partnership with ACS, as the sole awardee under the academic category.

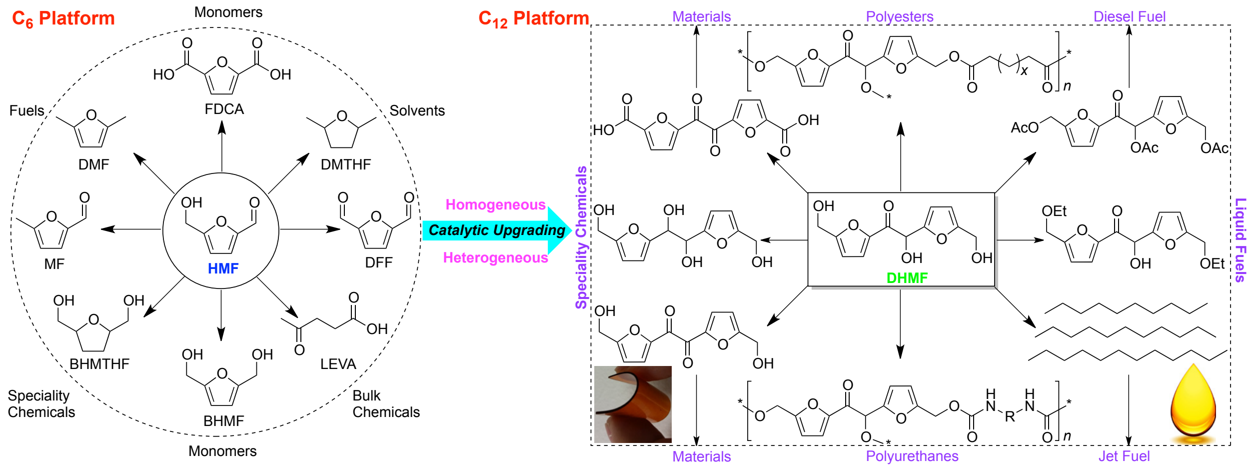


Fig. 1 Schematic summary of accomplishments achieved during the current grant period in developing the new C_{12} DHMF platform through quantitatively selective upgrading of HMF and subsequent catalytic transformations of DHMF into liquid fuels, specialty chemicals, and polymeric materials.

Description of Selected Eight Key Results of Work Accomplished during the Current Grant Period

1. Diesel and Jet Fuels from Biomass by Organocatalysis and Metal-Acid Tandem Catalysis [1]

We have developed a highly effective new strategy for upgrading biomass furaldehydes to liquid fuels. This strategy consists of organocatalytic self-condensation (umpolung coupling) of biomass furaldehydes into C_{10} and C_{12} furoin intermediates, followed by hydrogenation, etherification or esterification into oxygenated biodiesel (Fig. 1), and hydrodeoxygenation (HDO) by metal-acid tandem catalysis into premium alkane jet fuels (Fig. 2). The self-coupling step is carried out under solvent-free conditions, catalyzed by the organic NHC, and quantitatively selective and 100% atom-economical, all representing the hallmarks of a green process. Liquefying the C_{10} and C_{12} furoin intermediates can be readily accomplished by hydrogenation, etherification or esterification, producing oxygenated liquid biodiesel with considerably higher heat values than that of bioethanol. More significantly, premium hydrocarbon fuels were produced via the HDO of C_{12} DHMF in water under moderate conditions (300 °C, 3 h, 3.5 MPa H_2) with a bifunctional catalyst system (Pt/C + $TaOPO_4$), which yielded high quality alkane fuels with 96% selectivity to linear $C_{10\text{–}12}$ alkanes, consisting of 27.0 % *n*-decane, 22.9 % *n*-undecane, and 45.6 % *n*-dodecane (Fig. 2). The HDO catalyst can be recycled by simple filtration and the produced oil can be easily separated from the precursor DHMF aqueous phase.

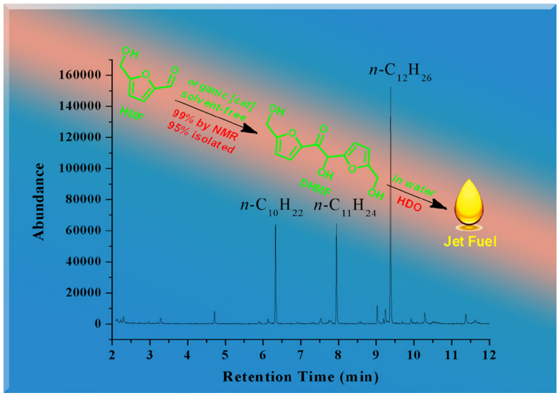
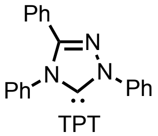


Fig. 2 GC-MS chromatogram of the organic phase products produced by the HDO of DHMF in water with Pt/C + $TaOPO_4$ and the overall process outlining the catalytic upgrading of the biorefining building block HMF to jet fuel with 96% selectivity to linear $C_{10–12}$ alkanes, consisting of 27.0 % *n*-decane, 22.9 % *n*-undecane, and 45.6 % *n*-dodecane. The discrete organic NHC catalyst employed for the HMF upgrading to DHMF is 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (TPT).



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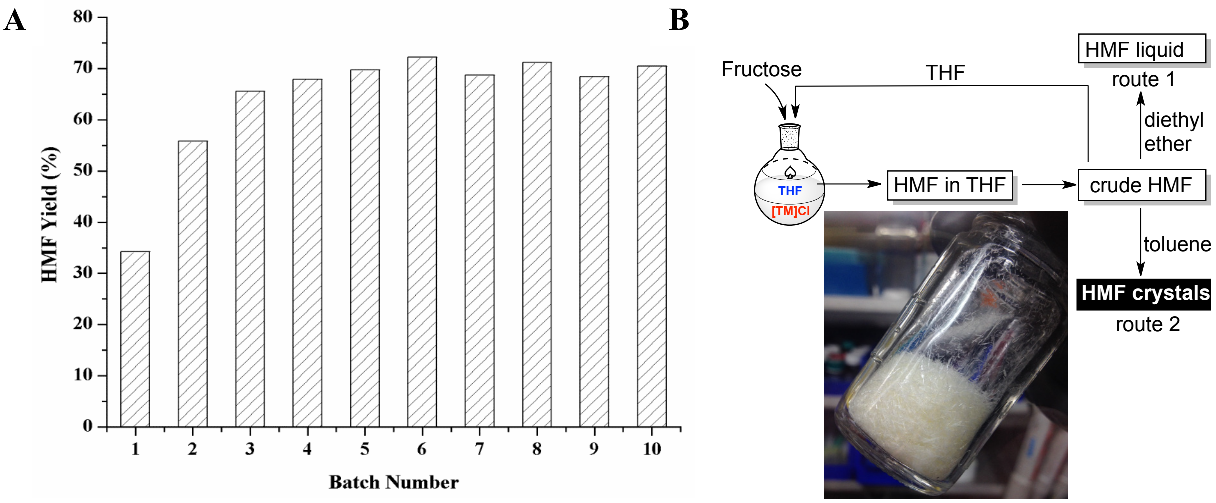
2. An Integrated Catalytic Process for Biomass Conversion and Upgrading to C_{12} Furoin and Alkane Fuel [2]

We have developed an integrated catalytic process for conversion and upgrading of biomass feedstocks into DHMF, through self-coupling of HMF via organocatalysis, and subsequently into *n*-$C_{12}H_{26}$ alkane fuel via metal-acid tandem catalysis. The first step of the process involves semi-continuous organocatalytic conversion of biomass (fructose, in particular) to the high-purity, crystalline HMF. Organic NHCs are found to catalyze glucose-to-fructose isomerization, and the relatively inexpensive thiazolium chloride [TM]Cl, a Vitamin B1 analog, catalyzes fructose dehydration to HMF of high purity (>99% by HPLC), achieving a constant HMF yield of 72% over 10 semi-continuous extraction batch runs (Fig. 3, **A**). Crystallization of the crude HMF from toluene yields the spectroscopically and analytically pure HMF as needle crystals (Fig. 3, **B**). The second step of the process is the NHC-catalyzed coupling of C_6 HMF produced by the semi-continuous process to C_{12} DHMF; the most effective organic NHC catalyst produces DHMF in 93% or 91% isolated yield with an NHC loading of 0.70 mol% or 0.10 mol% at 60 °C for 3 h under solvent-free conditions (Fig. 3, **C**). The third step of the process converts C_{12} DHMF to linear alkanes via HDO with a bifunctional catalyst system consisting of Pd/C + acetic acid + $La(OTf)_3$ at 250 °C and 300 psi H_2 for 16 h, producing liquid hydrocarbon fuel (78% alkanes), with a 64% selectivity to *n*-$C_{12}H_{26}$ and an overall C/H/O % ratio of 84/11/5.0 (Fig. 3, **D**).



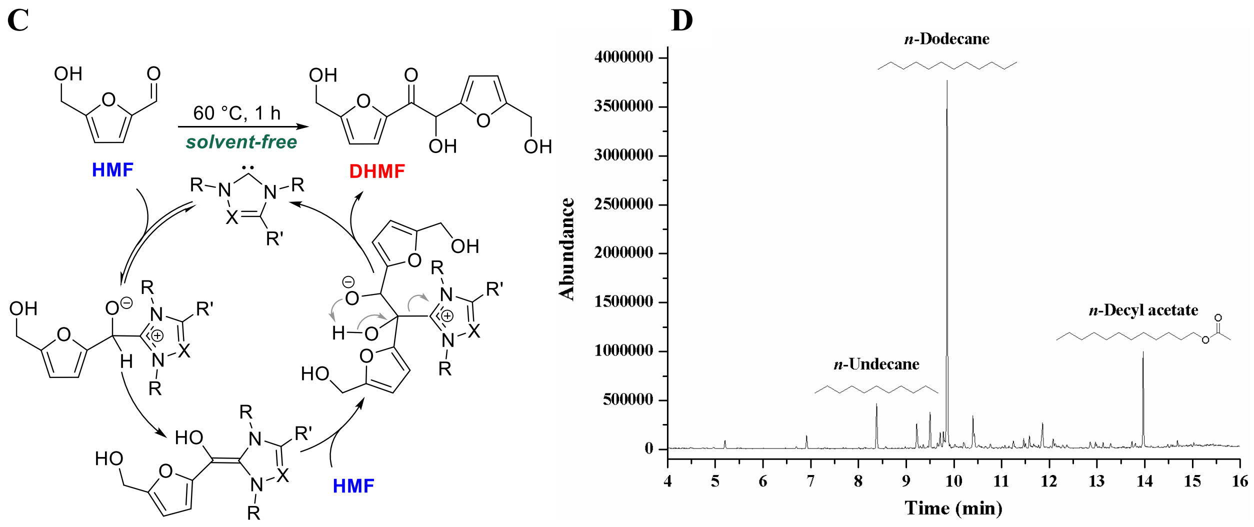


Fig. 3 **A**: HMF yields obtained from fructose conversion in [TM]Cl at 120 °C for 1 h by semi-continuous extraction with THF, shown as the average value of at least two runs with typical errors within ±3%. **B**: Integrated process for the production of the spectroscopically and analytically pure HMF from fructose catalyzed by [TM]Cl. **C**: Solvent-free NHC-catalyzed self-condensation of HMF to DHMF and depicted umpolung catalytic cycle. **D**: GC-MS chromatogram of the crude products (78% alkanes) produced by the HDO of DHMF in acetic acid catalyzed by Pd/C+ La(OTf)$_3$ at 250 °C under 300 psi H$_2$ for 16 h.

3. **Organocatalysis in Biorefining for Biomass Conversion and Upgrading** [3]

Organocatalysis using small-molecule organic compounds as catalysts has risen to prominence in organic synthesis and polymer synthesis. However, its application in biorefining for catalytic biomass conversion and upgrading into sustainable chemicals, materials, and biofuels has come to light only recently. This emergence of applying organocatalysis for biorefining has not only broadened the scope of organocatalysis and offered metal-free "green" alternatives for biomass conversion and upgrading, it has also showed some unique activity and selectivity in such transformations as compared to metal-mediated processes. This invited review captures highlights of this emerging area by focusing on utilization of organocatalytic means for catalytic conversions of cellulose, glucose and fructose, upgrading of furaldehydes, and organocatalytic polymerization of biomass feedstocks (Fig. 4).

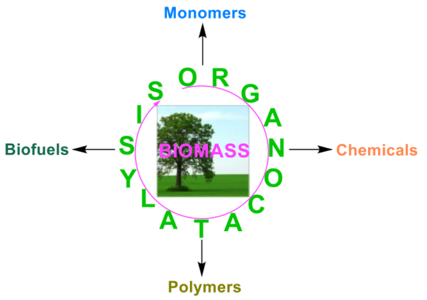


Fig. 4 Versatility of the "green" organocatalysis in biorefining for catalytic biomass conversion and upgrading into renewable chemicals, materials, and biofuels.

4. **Highly Active Organocatalysts for Upgrading of Furfural and HMF to C$_{10}$ and C$_{12}$ Furoins with Quantitative Selectivity/Yield and Atom-Efficiency** [5]

There is increasing interest in upgrading of C$_5$ furfural (FF) and C$_6$ HMF into C$_{10}$ and C$_{12}$ furoins as higher energy-density intermediates for renewable chemicals, materials, and biofuels. This work utilizes the organocatalytic approach, using the *in situ* generated *N,S*-heterocyclic carbene catalyst derived from readily available thiazolium ionic liquids (ILs), to achieve highly efficient self-coupling reactions of FF and HMF. Specifically, variations of the thiazolium IL structure have led to the *most active and efficient* *catalyst system to date*, which is derived from a new thiazolium IL carrying the electron-donating acetate group at the 5-ring position, ^{AcO}[TM]Cl (Fig. 5). Thus, for FF coupling by this IL (0.1 mol%, 60 °C, 1 h) in combination with Et_3N, C_{10} furoin was obtained in >99% yield. A 97% yield of the C_{12} furoin was also achieved from the HMF coupling by this catalyst system. On the other hand, the thiazolium IL bearing the electron-withdrawing group at the 5-ring position, ^{Ac}[TM]I, is the least active and efficient catalyst. The mechanistic aspects of the coupling reaction by the thiazolium catalyst system have also been examined and a mechanism has been proposed as shown in Fig. 5.

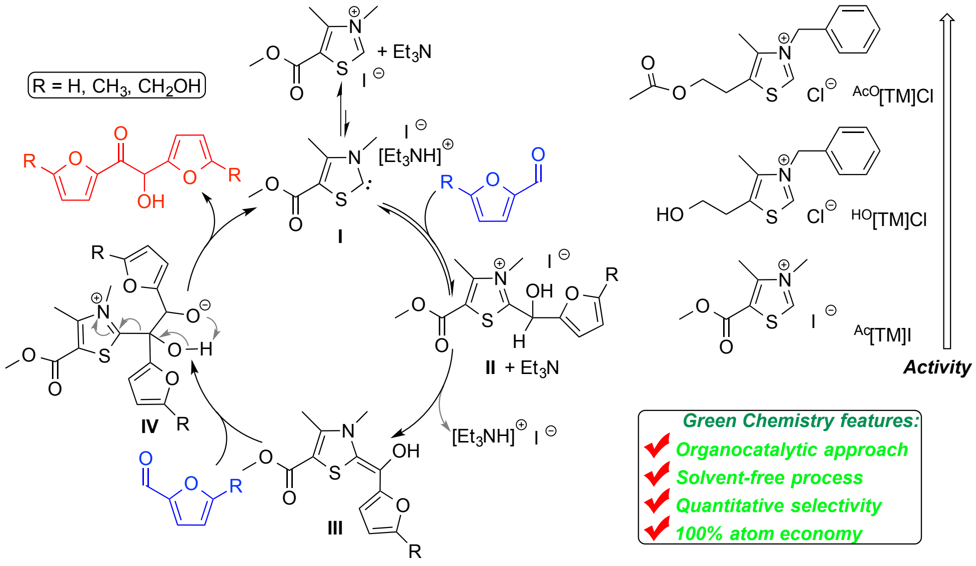


Fig. 5 Proposed mechanism for self-coupling of FF and HMF by ^{Ac}[TM]I/Et_3N and the activity trend.

5. Conversion of Biomass-Derived Furfuryl Methacrylate into Robust Cross-linked Materials [7]

Biomass-derived furfuryl methacrylate (FMA) has been effectively polymerized at ambient temperature by the P_4-phosphazene superbase, ^{t}Bu-P_4, with or without ^{i}PrOH as the co-initiator, producing syndio-rich atactic poly(furfuryl methacrylate), PFMA. The polymerization exhibits high initiation efficiencies up to 370% and is, therefore, a catalytic polymerization system. In the polymerization by ^{t}Bu-P_4 or ^{t}Bu-P_4 + ^{i}PrOH, the true initiator is shown to be 2-furfurylmethoxide, $[(C_4H_3O)CH_2O]^-$, generated from the reaction between FMA and ^{t}Bu-P_4 or $[^{t}Bu\text{-}P_4H]^+[^{i}PrO]^-$ during the induction period. The Diels-Alder (DA) "click" reaction has been utilized to produce two types of cross-linked PFMA materials. The first is PFMA–C_{60}, prepared from the DA reaction between the furfuryl group of PFMA and polydienophile C_{60} (Fig. 6, **A**), and the second employs a bifunctional bismaleimide (BM) to construct the cross-linked network polymer PFMA–BM (Fig. 6, **B**). When compared to the pristine PFMA, the cross-linked network polymers PFMA–C_{60} and PFMA–BM, especially the PFMA–BM materials with a high crosslinking density, exhibit significantly enhanced thermal stability at temperatures above 600 ºC and a much higher glass-transition temperature, as showed by thermal and thermomechanical analyses (Fig. 6, **C**).

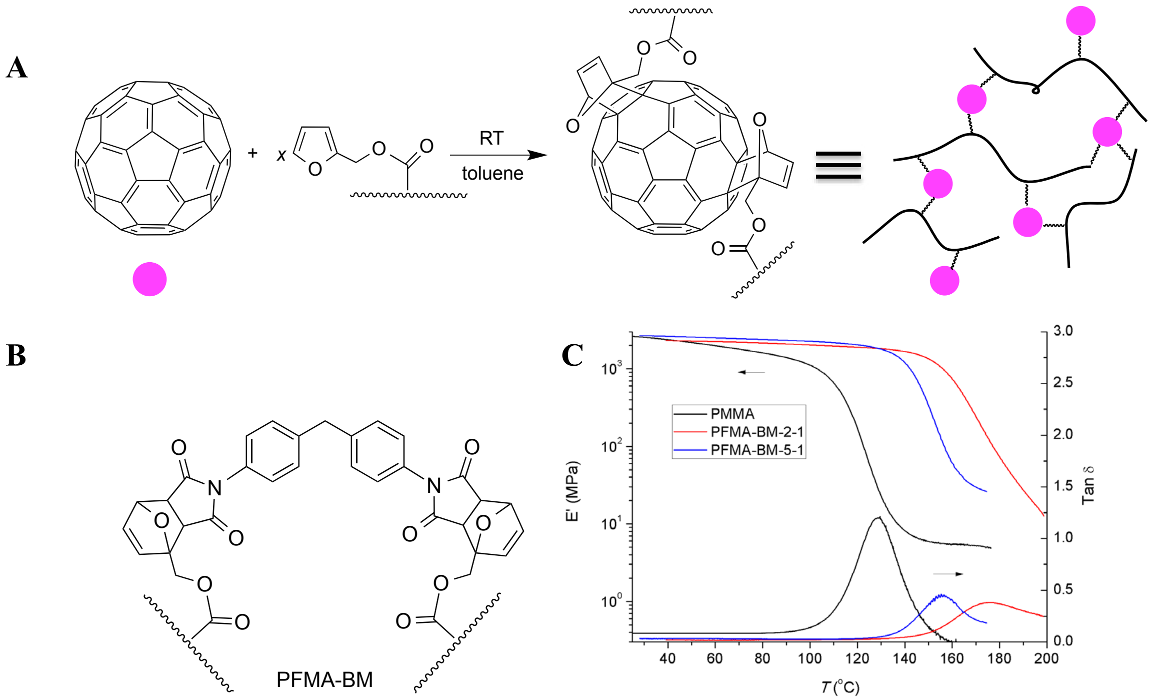


Fig. 6. Cross-linked PFMA-C_{60} material (**A**) by the DA "click" reaction of PFMA with C_{60}, cross-linked PFMA-BM polymers (**B**) through the DA "click" reaction, and dynamic mechanical analysis (DMA) curves of cross-linked PFMA materials (tension film mode): storage modulus (E') and tan δ (loss modulus E″/storage modulus E′) as a function of temperature (**C**).

6. An Interchangeable Homogeneous ⇔ Heterogeneous Catalyst System for Quantitative Furfural and HMF Upgrading [8]

A number of approaches have been developed to bridge homogeneous and heterogeneous catalysis, pursuing the ultimate goal of creating a catalytic system that can combine the best features of both homogeneous catalysis for high activity, efficiency and selectivity enabled by quantitative, discrete molecular catalyst sites *and* heterogeneous catalysis for ease of product separation and catalyst stability, recovery or recycling. Among which, heterogenization of homogeneous catalysts by supporting a molecular catalyst onto an insoluble inorganic or organic carrier is most common. Such heterogenized molecular catalysts perform catalytic reactions on the surfaces of insoluble carriers, often exhibiting different performances than the original molecular catalysts in a truly homogeneous environment. We hypothesized that a more desirable design would be a supported catalyst system that can release the molecular catalyst into solution for homogeneous catalysis on demand and then recover the catalyst back onto the support through *in situ* heterogenization after the reaction (Fig. 7). Such a catalyst release and recapture process can then be repeated for catalyst recyclability. To this end, intercalation of thiazolium cations $[TM]^+$ into the nanogalleries of Na^+/montmorillonite (MMT) clay leads to generation of recyclable supported precatalysts $[TM]^+$/MMT, which, upon treatment with a base, catalyze furfural self-condensation coupling reaction into furoin in almost constant yields of >97% over several cycles investigated. This catalyst system combines the best features of both homogeneous and heterogeneous catalyst systems, as it performs the homogeneous molecular catalysis by the discharged NHC catalyst in solution and then recovers the catalyst through *in situ* heterogenization after the reaction via re-intercalation of the charged precatalyst. The $[TM]^+$/MMT precatalysts which, upon activation with Et_3N, catalyze *rapid, selective, solvent-free* couplings of FF and HMF into the corresponding C_{10} and C_{12} furoins in 97%-99% and 97%-98% yield, respectively. Also noteworthy is that the catalysts can be readily recycled, showing no noticeable loss in their catalytic activity over four consecutive recycles. Thus, these desirable features possessed by the current catalyst system have enabled the development of the green and more environmentally benign process for the upgrading of FF and HMF.

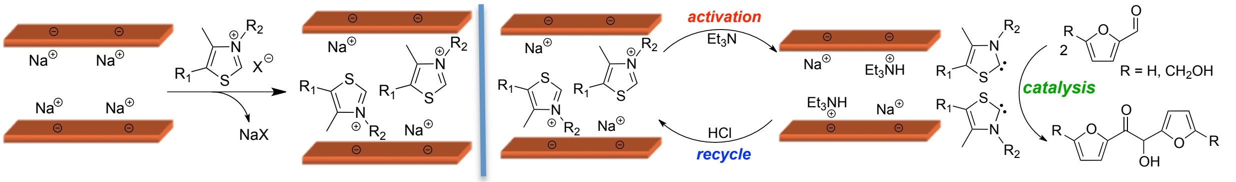


Fig. 7 Outlined synthesis of $[TM]^+$/MMT (left column) and schematic representation of the three processes involved in the self-coupling of FF by the MMT-supported catalysts (right column).

7. DHMF-Based Difuranic Polyols and Their Derived Linear and Cross-linked Polyurethanes [9]

Through catalytic upgrading of HMF, we have generated three difuranic polyol fine chemicals, including *triol* DHMF, *diol* 1,2-bis(5-(hydroxymethyl)furan-2-yl)ethane-1,2-dione (BHMF-dione), and *tetraol* 1,2-bis(5-(hydroxymethyl)furan-2-yl)ethane-1,2-diol (BHMF-diol), Fig. 8. These difuranic polyol monomers have been utilized in the polyaddition step-growth polymerization with various diisocyanates to produce bio-based linear or cross-linked polyurethane (PU) materials. More specifically, the triol DHMF was prepared from HMF in 95% yield via organocatalysis with an NHC catalyst precatalyst, TPT-OMe. Next, selective oxidation and reduction of DHMF afforded the diol monomer BHMF-dione and the tetraol monomer BHMF-diol, respectively. Catalyzed polyaddition of the diol BHMF-dione with various diisocyanates produced linear PUs, whereas catalyzed polyadditions using the triol and tetraol monomers led to crosslinked PUs (Fig. 9). Especially interesting is the PU material derived from BHMF-dione and aromatic diisocyanates such as diphenylmethane diisocyanate, which exhibited a number-average molecular weight (M_n) of 39.8 kg/mol, an onset decomposition temperature of 234 °C, a T_g of 140 °C, and a remarkably high amount of stable carbonaceous materials produced (~49%) when heated at > 600 °C. Various PU thin films have also been prepared by *in situ* polyaddition of these three polyols with diisocyanates in various ratios through solvent casting, affording PU materials ranging from being brittle to flexible with a relatively high strain at break of 300% (Fig. 9, **B**(d)).

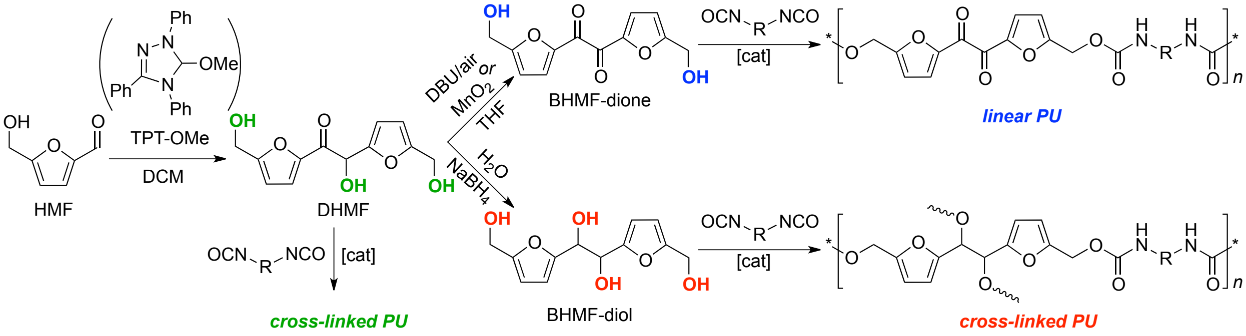


Fig. 8 Outlined synthesis of fine chemicals by HMF upgrading to triol DHMF, diol BHMF-dione, and tetraol BHMF-diol, as well as their derived linear and cross-linked PU materials.

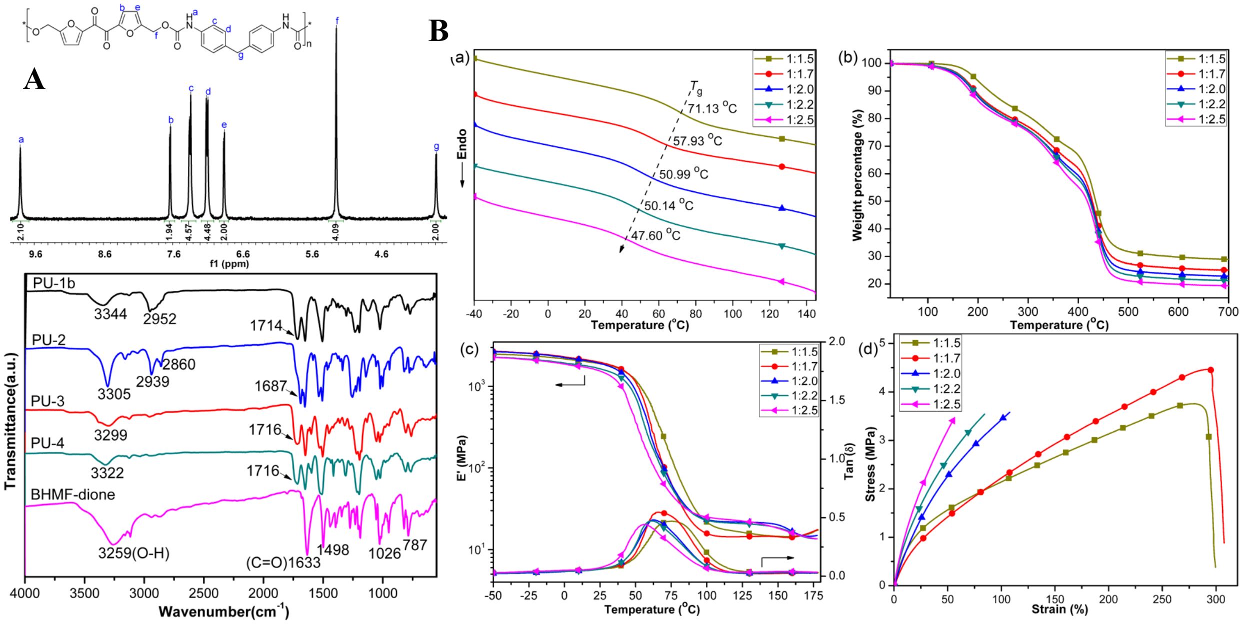
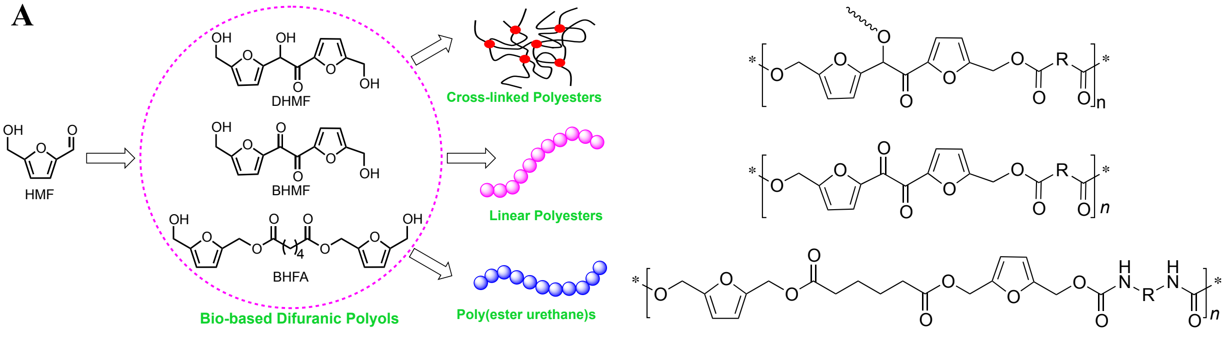


Fig. 9 **A**: ^{1}H NMR (DMSO-d_6) of the linear PU produced from polyaddition of BHMF-dione and diphenylmethane diisocyanate (top) and FTIR spectra of BHMF-dione monomer and its derived linear PUs (bottom). **B**: Differential scanning calorimetry (DSC) curves (a), thermogravimetric analysis (TGA) curves (b), dynamic mechanical analysis (DMA) curves (c), and stress-strain curves (d) of PU films derived from DHMF and hexamethylene diisocyanate.

8. HMF-Derived Linear and Crosslinked Polyesters and Poly(ester-urethane)s [10]

To investigate the impact of rigid and flexible difuranic polyols on the resulting polyester (PE) and poly(ester-urethane) (PEU) properties, we employed three bio-based difuranic polyol monomers, 5,5'-bihydroxymethyl furil (BHMF), DHMF, and bis[5-(hydroxymethyl)furan-2-yl]methyl]adipate (BHFA), all derived from the biomass platform chemical HMF, for the synthesis of a series of new linear and cross-linked PEs as well as amorphous and semicrystalline PEUs (Fig. 10, **A**). The polycondensations of diols (rigid BHMF and flexible BHFA) with various diacyl chlorides afford linear PEs, whereas the rigid triol (DHMF) reacts with diacyl chlorides to form cross-linked PEs. Among these difuranic PEs, the most intriguing PE is the one containing C=C double bonds, derived from BHFA and fumaryl chloride, which exhibits the unique self-curing ability via the Diels-Alder reaction (Fig. 10, **B**). Furthermore, the catalyzed polyaddition of BHFA with various diiscyanates produces novel PEUs, the most interesting of which is the one derived from BHFA and hexamethylene diisocyanate (PEU-1), a semicrystalline material displaying a high melting-transition temperature of 135.8 °C (Fig. 10, **C**).



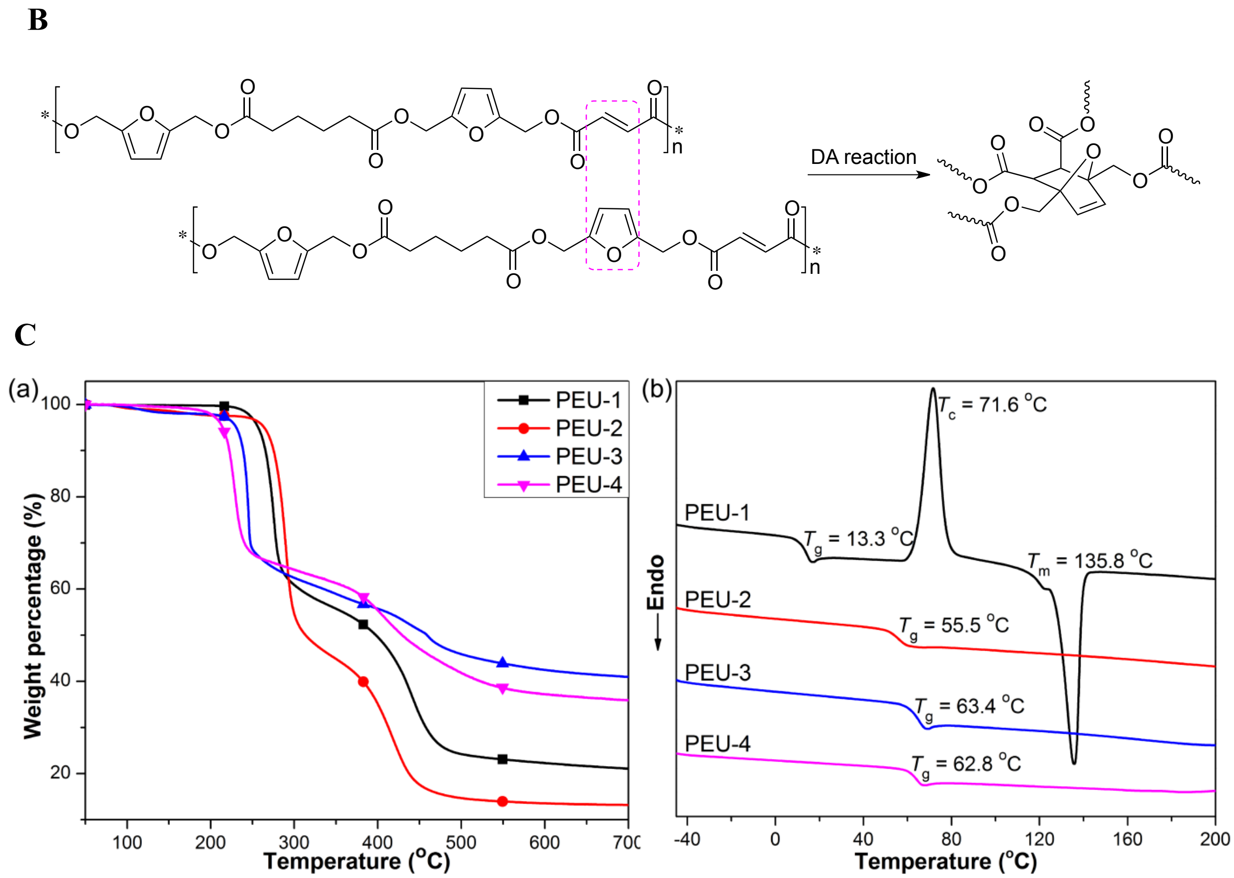


Fig. 10 **A**: Outlined synthesis of new linear and cross-linked PEs as well as amorphous and semicrystalline PEUs using bio-difuranic polyol monomers derived from HMF. **B**: Schematic representation of self-curing of PE, derived from BHFA and fumaryl chloride, through the Diels-Alder reaction. **C**: TGA curves (a) and DSC curves (b) of PEUs derived from BHFA with various diisocyanates: hexamethylene diisocyanate (PEU-1), isophorone diisocyanate (PEU-2), 2,4-toluenediisocyanate (PEU-3), and diphenylmethane diisocyanate (PEU-4).

9. Organocatalytic Cross-coupling of FF and HMF to Multifunctional Difuranic C_{11} Building Blocks [11]

Having achieved highly efficient homo-couplings of FF and HMF into C_{10} and C_{12} furoins, respectively, next we turned out attention to develop possible selective cross-coupling between FF and HMF into C_{11} furoins. Such C_{11} furoins can exist as two structural isomers and possess three reactive sites (two hydroxyl groups and one nucleophilic carbon at the 5-position of the furan ring, Fig. 11), thus serving as potential *tri-functional C_{11} difuranic building blocks* for biopolymers and biofuels. We found that NHC-catalyzed coupling reaction of FF and HMF in solution gives a statistical mixture of products including homo-coupled C_{10} and C_{12} furoins as well as cross-coupled C_{11} furoins, regardless of the electronics or sterics of the NHC pre-catalyst used, but a slight preference for cross-coupled products (~60%) under neat conditions has been achieved. The two cross-coupled products, new C_{11} furoins, have been isolated in 48.1% yield and further separated into their pure state in 22.2% and 19.9% yield, respectively. The isolated C_{11} furoins have been fully characterized by NMR, HRMS, and single crystal X-ray diffraction. A simple metal-free/in-air oxidation reaction with the organic base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) converts these two isomeric furoins into the single α-diketone furanil structure, another new C_{11} bio-derived building block (Fig. 11). Worth noting here is that a mixture containing various, but quantifiable, amounts of four C_{10}-C_{12} furoins could be used directly without separation as an *intriguing mixed feedstock* for the synthesis of liquid fuels and useful resin materials.

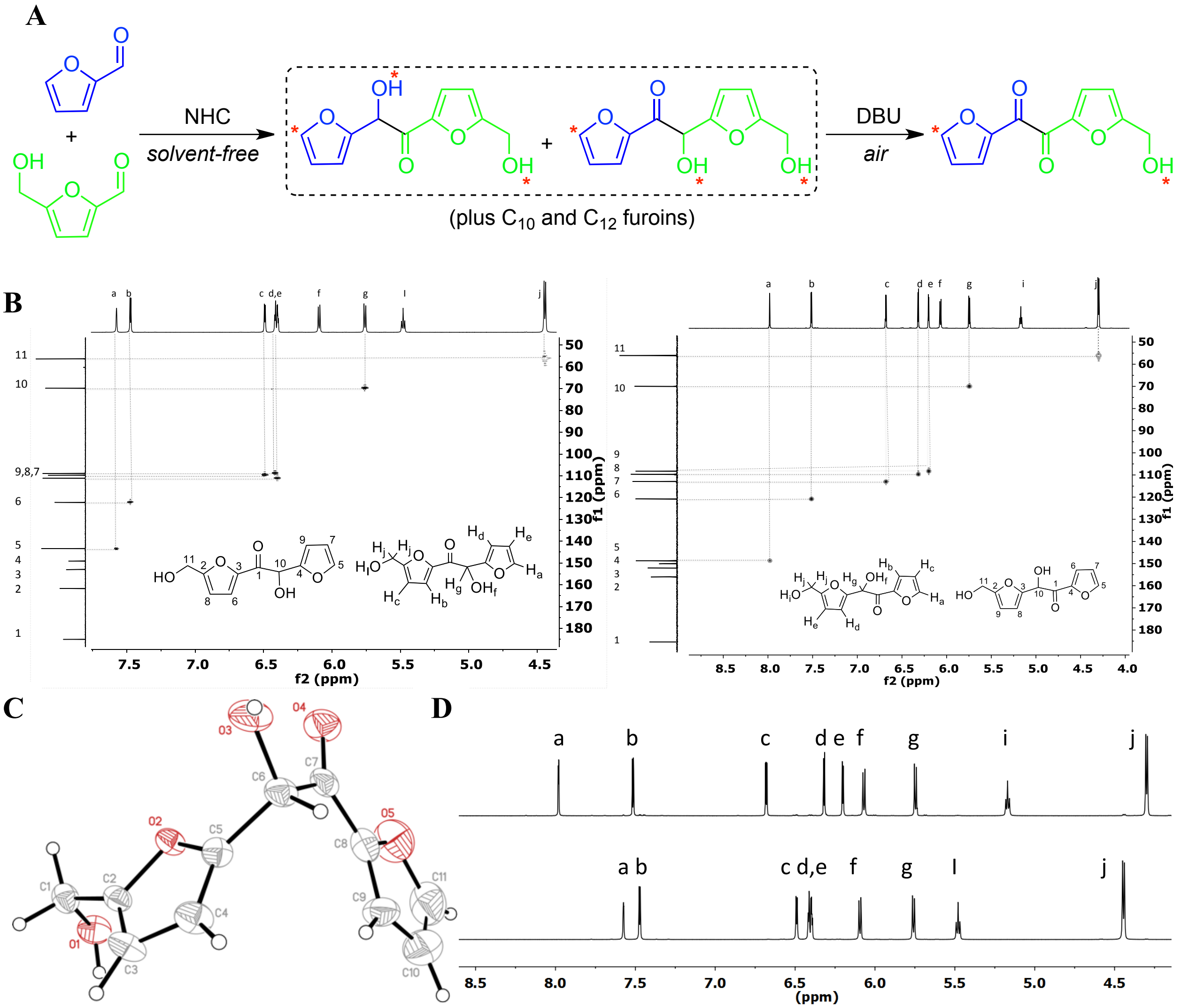


Fig. 11 **A**: NHC-catalyzed cross-coupling of FF and HMF to produce two new C_{11} furoins or *α*-hydroxy-ketones, plus homo-coupled C_{10} and C_{12} furoins, and selective metal-free oxidation of C_{11} furoins to the α-diketone product. **B**: HSQC spectrum (DMSO-d_6, 25 °C) of the two C_{11} furoins showing ^1H–^{13}C signal correlation between adjacent nuclei. **C**: Structural confirmation of one C_{11} furoin isomer (*worth noting here is that it is important to structurally characterize at least one of the C_{11} furoins by X-ray diffraction, because of the uncertainty about the spectroscopic characterization due to their very subtle differences in the structure*). **D**: Overlay and assignments of ^1H NMR spectra (DMSO-d_6, 25 °C) of the two C_{11} furoins.

10. Recyclable Earth-Abundant Metal Nanoparticle Catalysts for Selective Transfer Hydrogenation of Levulinic Acid to Produce *γ*-Valerolactone [12]

In this contribution we reported that metal-nanoparticles (M-NPs), *in situ* generated via thermolysis or microwave irradiation of earth-abundant M(0) (M = Fe, Co, Cr) carbonyls, catalyze selective transfer hydrogenation/lactonization of levulinic acid (LA) to *γ*-valerolactone (GVL) in 93% isolated yield (by Fe-NPs derived from $Fe_3(CO)_{12}$, in the presence of 4 equiv. of formic acid (FA) and 1.0 equiv. of Et_3N, using H_2O as solvent). Overall, these earth-abundant M-NP catalysts performed as well as the precious metal Ru-NPs for the LA hydrogenation. Several lines of evidence clearly indicated the presence and direct involvment of M-NPs in this LA-to-GVL conversion system via catalytic transfer hydrogenation.

The TEM images of the reaction sample withdrawn from the solution at the end of the transfer hydrogenation of LA using $Co_2(CO)_8$ clearly revealed the existence of monodisperse small Co-NPs with an average size of NPs(100) of 2.2 ± 0.4 nm. Furthermore, EDS spectrum of Co-NPs obtained using the post LA-to-GVL reaction sample employing $Co_2(CO)_8$ revealed no cobalt oxide formation or oxygen associated with Co. Additional poisoining experiments further verified the M-NP catalyst being responsible for the catalytic activity observed for the LA-to-GVL conversion. To examine the recyclability of the earth-abundant M-NP catalysts, we preformed the Co-NPs derived from $Co_2(CO)_8$ via microwave irradiation and stabilized by poly(vinylpyrrolidone) (PVP) and poly(methyl methacrylate) (PMMA). TEM images of Co-NPs/PVP (Fig. 12) and Co-NPs/PMMA confirmed the formation of the corresponding M-NPs with an average size of NPs(100) = 7.4 ± 1.5 nm for Co-NPs/PVP or 5.3 ± 2.0 nm for Co-NPs/PMMA. EDS spectrum of the preformed Co-NPs/PVP with EtOH as the solvent also revealed no cobalt oxide formation or oxygen associated with Co. In the presence of 2.0 equiv. of KOH and using EtOH as both the solvent and hydrogen source, the catalysis results showed that the polymer-stabilized Co-NPs gave a higher isolated GVL yield than that by the *in situ* generated Co-NPs. More importantly, the polymer-supported/stabilized catalyst Co-NPs/PMMA showed excellent recyclability, with essentially constant LA conversions of 98 – 97% and isolated GVL yields of 85 – 84% (Fig. 12) achieved for all the five cycles performed. Impressively, pre-generation of M-NPs via microwave irradiation greatly enhances the rate of the conversion, enables the use of ethanol as both the solvent and hydrogen source for the selective reduction of LA to GVL without forming the undesired ethyl levulinate, and affords recyclable polymer-supported/stabilized NPs.

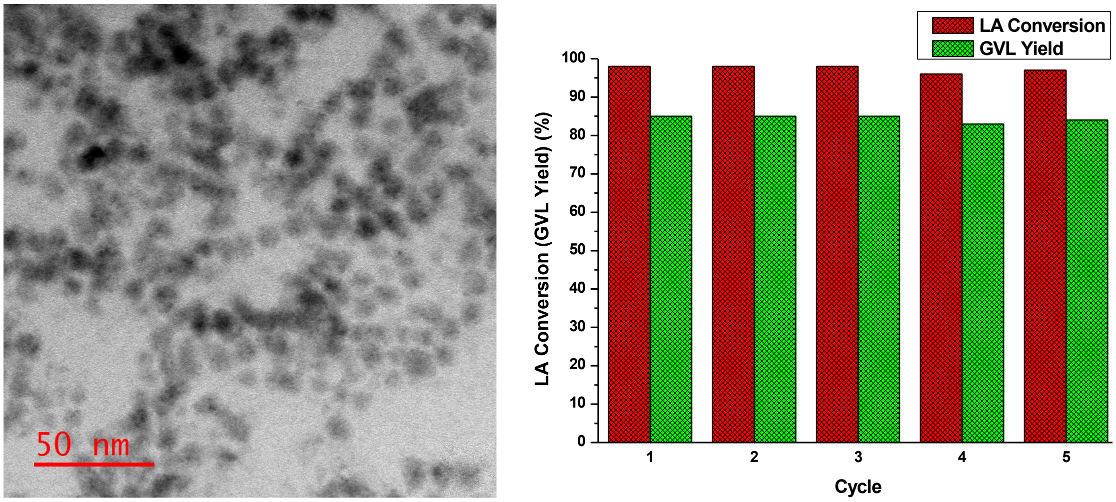


Fig. 12 TEM image of Co-NPs/PVP with an average size of NPs(100) = 7.4 ± 1.5 nm and recyclability test of the Co-NPs/PMMA in the LA-to-GVL conversion via transfer hydrogenation using EtOH as both the solvent and hydrogen source: red columns, LA conversion = ~98%; green columns, isolated GVL yield = ~85%.

Impact on Science and Technologies of Relevance to DOE

This project seeks to develop efficient, selective, and cost-effective catalytic systems for upgrading of key biomass-derived building blocks into value-added chemicals, polymeric materials, and liquid fuels. Hence, the research described in this proposal addresses one of the DOE-BES's priority research directions in Catalysis for Energy, Value-added Chemical, and Materials, particularly in terms of exploring new catalytic pathways for efficient lignocellulosic biomass conversion and upgrading into chemicals, materials, and fuels. The technology we developed for the organocatalytic upgrading of the key biorefining building block C_6 HMF into C_{12} DHMF as a kerosene/jet or diesel fuel intermediate, which performs the umpolung condensation coupling under solvent-free conditions, uses ionic liquids or NHCs as organic catalysts, and achieves quantitative selectivity and 100% atom-economy, *was awarded an issued US patent and won the 2015 Presidential Green Chemistry Challenge Award sponsored by EPA in partnership with ACS.*

Unexpended Balance

There were no residual funds at the end of the current grant and NCE period.

Peer-Reviewed Publications Based on the Current DOE Funding Period

[1] Liu, D.; Chen, E. Y.-X. "Diesel and Alkane Fuels from Biomass by Organocatalysis and Metal-Acid Tandem Catalysis", *ChemSusChem* **2013**, *6*, 2236–2239.

[2] Liu, D.; Chen, E. Y.-X. "An Integrated Catalytic Process for Biomass Conversion and Upgrading to C_{12} Furoin and Alkane Fuel", *ACS Catal.* **2014**, *4*, 1302–1310.

[3] Liu, D.; Chen, E. Y.-X. "Organocatalysis in Biorefining for Biomass Conversion and Upgrading", *Green Chem.* **2014**, *16*, 964–981 (*invited review*).

[4] Zhang, Y.; Chen, E. Y.-X. "Polymerization of Nonfood Biomass-Derived Monomers to Sustainable Polymers", *Top. Curr. Chem.* **2014**, *353*, 185–227 (*invited contribution to the topics volume on Selective Catalysis for Renewable Feedstocks and Chemicals*).

[5] Zang, H.; Chen, E. Y.-X. "Organocatalytic Upgrading of Furfural and 5-Hydroxymethyl Furfural to C_{10} and C_{12} Furoins with Quantitative Yield and Atom-Efficiency", *Int. J. Mol. Sci.* **2015**, *16*, 7143–7158 (*invited contribution to the Green Chemistry and Biorefinery issue*).

[6] Magnusson, C. D.; Liu, D.; Chen, E. Y.-X.; Kelland, M. A. "Non-Amide Kinetic Hydrate Inhibitors: Investigation of the Performance of a Series of Polyvinylphosphonate Diesters", *Energy & Fuels* **2015**, *29*, 2336–2341.

[7] Feng, S.; Schmitt, M.; Chen, E. Y.-X. "Organocatalytic Polymerization of Furfuryl Methacrylate and Post Diels-Alder Click Reaction to Cross-linked Materials", *Macromol. Chem. Phys.* **2015**, *216*, 1421−1430.

[8] Yan, B.; Zang, H.; Jiang, Y.; Yu, S.; Chen, E. Y.-X. "Recyclable Montmorillonite-supported Thiazolium Ionic Liquids for High-yielding and Solvent-free Upgrading of furfural and 5-Hydroxymethylfurfural to C_{10} and C_{12} Furoins", *RSC Adv.* **2016**, *6*, 76707−76715.

[9] Mou, Z.; Feng, S.; Chen, E. Y.-X. "Bio-based Difuranic Polyol Monomers and Their Derived Linear and Cross-linked Polyurethanes", *Polym. Chem.* **2016**, *7*, 1593−1602.

[10] Mou, Z.; Chen, E. Y.-X. "Polyesters and Poly(ester-urethane)s from Bio-based Difuranic Polyols", *ACS Sustainable Chem. Eng.* **2016**, *4*, 7118−7129.

[11] Wilson, J.; Chen, E. Y.-X. "Organocatalytic Cross-coupling of Bio-furanics to Multifunctional Difuranic C_{11} Building Blocks", *ACS Sustainable Chem. Eng.* **2016**, *4*, 4927−4936.

[12] Gowda, R. R.; Chen, E. Y.-X. "Recyclable Earth-Abundant Metal Nanoparticle Catalysts for Selective Transfer Hydrogenation of Levulinic Acid to Produce γ-Valerolactone", *ChemSusChem* **2016**, *9*, 181−185.

Issued US Patent: Chen, E. Y.-X.; Liu, D. "Biorefining Compounds and Organocatalytic Upgrading Methods", U.S. Pat. 9,469,626 B2, **2016**.