CHAPTER 1

PRODUCTION OF RENEWABLE TEREPHTHALIC ACID USING DIELS-ALDER REACTIONS WITH ETHYLENE

1.1 Motivation for renewable terephthalic acid and overview of current approaches for its production.

Purified terephthalic acid (PTA) and ethylene glycol (EG) are used as monomers in the production of the important and large-scale polymeric material, poly(ethylene) terephthalate (PET). PET is used in a wide range of applications, from food and drink packaging to synthetic fibers for clothing and textiles. PTA and EG have been historically produced from petroleum. PTA is almost solely produced from the oxidation of p-xylene (PX) in the liquid phase by the Amoco process[1,2], and PX is produced by the catalytic reforming of gasoline-type streams in oil refineries. Ethylene produced from catalytic cracking processes in oil refineries can be oxidized to ethylene oxide, which in turn is hydrolyzed to EG.

The rising price of crude oil has influenced the choice of feedstock for chemical producers and has led to the development of processes for the production of renewable, biomass-derived chemicals.[3] These chemicals can be grouped into two families of bio-chemicals: (1) a “drop-in” chemical that is chemically identical to a petroleum-based chemical and is meant to supplement or replace it, or (2) a chemical that is new and different than any petroleum-based chemical on the market. The first family of biochemicals are generally easier to develop and produce on a commercial scale since a market for the chemical is already in place.

Renewable bio-PET is one example of a chemical belonging to this first family. The successful use of corn and sugarcane-based ethanol as a feedstock for the production of bio-EG for the production of PET has allowed for a PET material that is ~30 wt % biobased. In this process, the bio-ethanol is converted to ethylene by dehydration followed by oxidization to ethylene oxide and hydrolysis to EG, analogous to how EG is normally produced. PET producers have been able to sell and market this material as “bio-PET”, although only the EG portion is renewable. There is a desire to produce completely, 100% renewable PET and, therefore, a demand for new technologies for the production of renewable, biomass-derived PTA.[4]

One important technology that has been developed by a Colorado-based company, Gevo, Inc., is a process to produce PX from sugars using a biological conversion step.[4] Gevo utilizes a microorganism that has been engineered for the fermentation of glucose into isobutanol. Isobutanol is dehydrated to isobutene and dimerized to diisobutylene. Diisobutylene undergoes dehydrocyclization to PX that is finally converted to PTA via the traditional oxidation process. Although the dehydrocyclization step can produce PX from diisobutylene at >85% selectivity, the overall theoretical mass yield of PTA is only 46% since 1/3 of the carbon in the initial glucose is lost as CO_2 in the fermentation step to produce isobutanol. Ultimately, this results in two glucose molecules being required to make only one PTA molecule.

Another important technology being pursued commercially by the California-based company, Micromidas, and the Michigan Molecular Institute

(MMI) is the production of PX from cellulosic biomass and utilizes Diels-Alder reactions between ethylene and a biomass-derived intermediate, 2,5-dimethylfuran (DMF). The company has developed methods of converting inexpensive waste cellulosic biomass into the intermediates, 5-(hydroxymethyl)furfural (HMF) and 5-(chloromethyl)furfural (CMF), by using hydrochloric acid as catalyst.[5] HMF and CMF undergo a H_2 reduction step to DMF, and DMF is further reacted with ethylene gas at high pressure (30 – 70 bar) and temperature (225-300 ^oC) to produce PX through a Diels-Alder-dehydration reaction (Fig. 1.1). The Diels-Alder-dehydration reaction has been optimized with the use of a homogeneous Lewis acid catalyst to produce PX in high yields (>95% based on DMF) within short reaction times.[6] If the ethylene gas used in the Diels-Alder step is derived from biomass (e.g., dehydration of bio-ethanol), then the final PX and PTA is 100% biobased. This route is able to efficiently convert HMF/CMF and ethylene to PX by conserving all the carbon in the HMF/CMF and ethylene molecules, giving a theoretical mass yield (for carbon) of 100%.

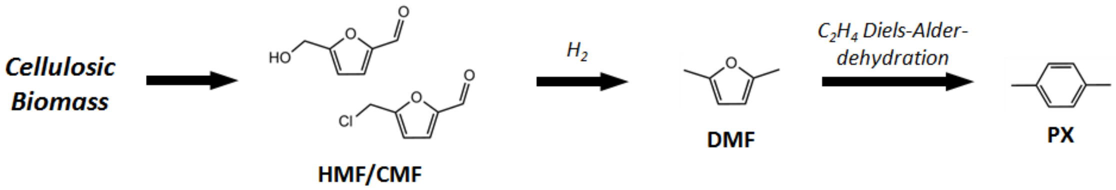

Fig. 1.1 Micromidas/MMI pathway from biomass to PX.

The Diels-Alder-dehydration reaction actually consists of two steps: (1) a reversible Diels-Alder cycloaddition between DMF and ethylene and (2) a dehydrative aromatization of the oxabicyclic cycloadduct (Fig. 1.2). A UOP patent first reported the conversion using a variety of catalytic materials.[7] The use of Bronsted acid zeolites[8-15] and WO_x-ZrO_2[16] as catalysts for the conversion have been the focus of several recent investigations.

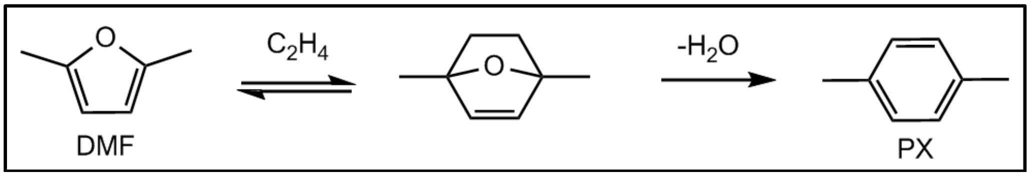

Fig. 1.2 Diels-Alder-dehydration reaction for the conversion of DMF and ethylene to PX.

The one-step conversion of raw cellulosic biomass to the HMF/CMF intermediates that the Micromidas/MMI pathway utilizes is similar to another process that has been commercialized by a Swiss chemical company, AVA Biochem. AVA Biochem's process converts waste cellulosic biomass into 5-hydroxymethylfurfural (HMF) in a one-step hydrothermal carbonisation (HTC) process.[17] In early 2014, AVA Biochem announced that it was producing HMF in Switzerland at 20 tons per year for industrial and research customers. These examples of Micromidas/MMI and AVA Biochem producing HMF or CMF in a single hydrothermal step suggests good economic viability of producing biobased chemicals via the HMF/CMF intermediates, and may be more competitive than biological-based processes, such as Gevo's fermentation-based process for the production of the isobutanol intermediate.

There are numerous other reports in the literature of methods for producing the intermediate HMF from biomass feedstocks.[18,19] One recent example was published by the M.E. Davis group in 2011 for the production of HMF from glucose and starch.[20] The system utilized a two-step conversion that was performed in a single batch reactor. The first step was the isomerization of glucose to fructose in aqueous media catalyzed by a Lewis acidic Beta molecular sieve with tin incorporated into the framework (Sn-Beta) and the second step was the HCl-catalyzed dehydration of fructose to HMF. An organic extraction phase was present to remove HMF from the reacting aqueous phase as it was formed. This system was shown to produce HMF from glucose or starch with high selectivity (69-72 %) at high conversions (>75 %).

1.2 Current Diels-Alder routes for upgrading HMF and ethylene to PTA.

Most of the work relating to the conversion of HMF (or CMF) to PTA has involved the production of PX via the Diels-Alder-dehydration reaction between DMF and ethylene. As discussed above, Micromidas and MMI have developed an efficient process for this Diels-Alder-dehydration step using homogeneous Lewis acid catalysts.[6] Alternatively, this step may be catalyzed by a variety of other materials as well, including Bronsted acid zeolites (e.g., H-Y, H-Beta), acetic acid, WO_x-ZrO_2, activated carbon, silica gel and γ-alumina.[7-16, 21] The reactions are performed in batch pressure reactors in the liquid phase under an ethylene atmosphere. The temperatures are typically 200-300°C with pressures between 30-70 bar.

A significant disadvantage to a route involving DMF in the Diels-Alder-dehydration step is the requirement for the conversion of HMF (or CMF) to DMF. This step requires a source of H_2 gas for the reduction and expensive metal reduction catalysts (e.g., CuRu/C). The source of H_2 and the cost of the reduction catalyst is an important consideration. In one calculation, the reduction catalyst cost contributed to over 40% of the total capital cost of a PX plant utilizing the DMF intermediate.[22] A pathway to PTA that avoids a H_2 reduction step may be advantageous.

One route that has been proposed that avoids the reduction step to DMF has been published in the patent literature. This route begins with the *oxidation* of HMF, rather than reduction, to the intermediate 2,5-furandicarboxylic acid (FDCA).[21, 23] FDCA can be obtained quantitatively from HMF by air oxidation.[24]

Although FDCA has been shown to react with ethylene to produce PTA via the Diels-Alder-dehydration reaction (Fig. 1.3), only low yields have been reported. The benefits to this route compared to going through the DMF intermediate are (1) it does not require an expensive reduction step and (2) the Diels-Alder-dehydration product is PTA rather than PX.

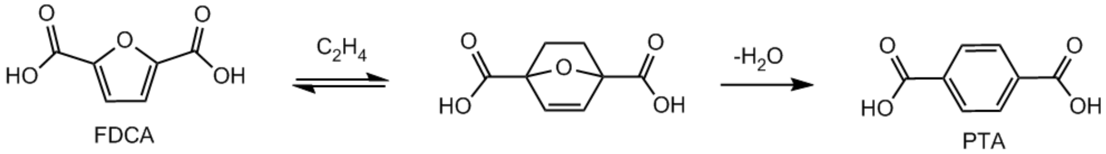

Fig. 1.3 Diels-Alder-dehydration reaction for the conversion of FDCA and ethylene to PTA.

Unfortunately, the conversion of FDCA and ethylene to PTA is very slow and only provides low yields of PTA. In one example, a PTA yield of 0.14 mol % is reported after reaction for 2 hours in aqueous solvent.[23] By performing the reaction in acetic acid, which behaves as both a solvent and weak dehydration catalyst, a 16.5 mol % yield of PTA was achieved after 32 hours of reaction.[21] The selectivity in both of these examples were not reported.

It is not surprising that the reaction between FDCA and ethylene is slow and difficult. The theory behind the mechanism of a Diels-Alder reaction describes the interaction of the molecular orbitals between the diene and the dienophile.[25] Diels-Alder cycloaddition reactions can be grouped into two types – Normal electron demand Diels-Alder reactions and Inverse electron demand Diels-Alder reactions. Normal electron demand reactions are the most common and involve an “electron-rich” diene and an “electron-poor” dienophile. In these reactions, the HOMO of the diene overlaps with the LUMO of the dienophile. The more efficient the overlap between the orbitals, or the more similar the energies, the easier the reaction proceeds, and substituents on the molecules contribute to the energies of these orbitals. Electron-donating groups bound to the diene will tend to raise the energy of the HOMO orbital of the molecule, and electron-withdrawing groups bound to the dienophile tend to lower the LUMO energy of the molecule. For example, ethylene is taken to be the simplest dienophile and, since it is lacking any electron-withdrawing groups, ethylene is also known to be quite inactive in Diels-Alder reactions, requiring elevated reaction temperatures and long reaction times. If an electron-withdrawing group is attached to the dienophile function (e.g., methyl acrylate), the dienophile becomes significantly more active in Diels-Alder reactions.

In the Diels-Alder cycloaddition between FDCA and ethylene, the dienophile, ethylene, is not the only inactive reactant. The diene in this case, FDCA, is also inactive due to the carboxylic acid groups (strongly electron withdrawing) on the 2- and 5- positions that cause the diene function to become “electron-poor” by lowering the energy of the HOMO. Examples of furan Diels-Alder chemistry in which the furanic diene contains carboxylate groups are rare.[26] Other than the above examples regarding the reaction of FDCA with ethylene to produce PTA in low yields, known examples that have been found in the literature involve (1) 5-amino furoates reacting with dienophiles at elevated temperatures[27,28] and (2) furoic acid reacting with monomeric cyclopentadienone.[29]

1.3 Research objective of the current thesis

Although the conversion of HMF to PTA based on the DMF/ethylene/PX Diels-Alder-dehydration reaction is possible and several effective catalysts exist for the Diels-Alder-dehydration step, the reduction step to convert HMF/CMF to DMF requires a H_2 source (three moles of H_2 per mol of HMF) and expensive metal reduction catalysts. A route that avoids the reduction step to DMF and, instead, converts HMF itself or a HMF derivative to the PTA presursor may be advantageous.

The main research objective in this thesis was to develop a new catalytic Diels-Alder route for the conversion of biomass-derived HMF to PTA, and avoid the reduction of HMF to DMF. Along with the production of biomass-derived EG, the new technology will allow for the production of 100% biobased PET.

The strategy for approaching this objective will involve exploratory research for (1) new Diels-Alder-dehydration reactions between oxygenated furans and ethylene and (2) new catalysts for these new reactions (Fig. 1.4). The following two sections will further discuss these areas, that is the proposed catalysts that were of particular interest and the new chemical reactions that were proposed to allow for novel routes to PTA from HMF.

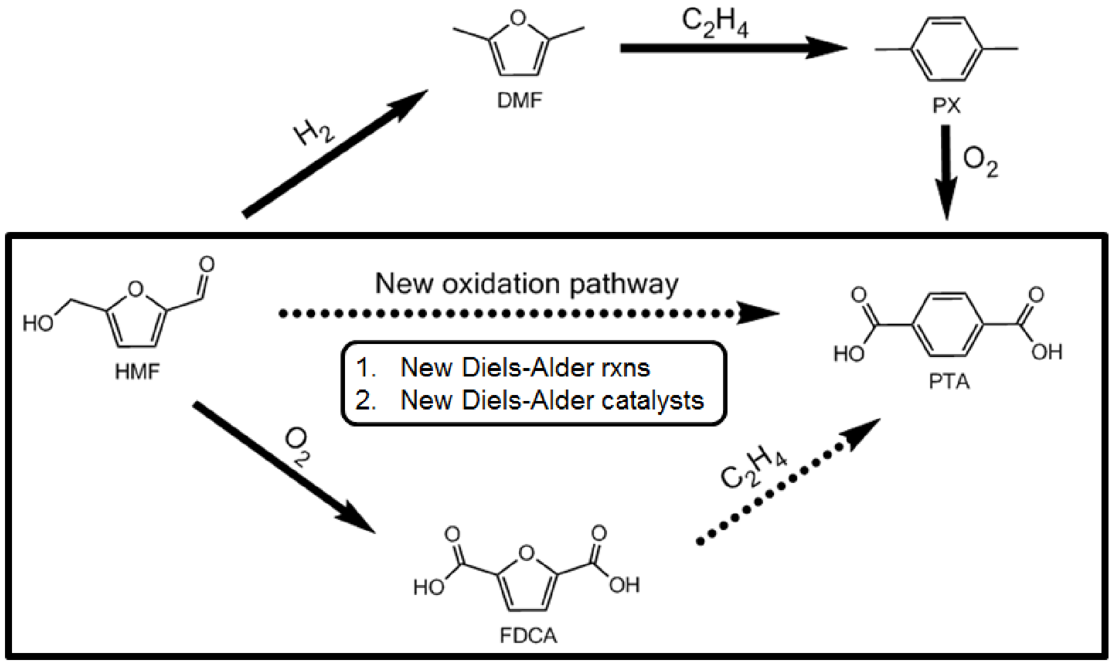

Fig. 1.4 Approach for developing new catalytic Diels-Alder route for the conversion of biomass-derived HMF to PTA.

1.4 Lewis acid molecular sieves as potential Diels-Alder-dehydration catalysts

The Diels-Alder-dehydration reaction between a furanic diene and ethylene to generate the substituted aromatic product and water involves two reactions in tandem. The Diels-Alder cycloaddition between the furan and ethylene produces an oxabicyclic intermediate, and is followed by the dehydrative aromatization of the oxabicyclic to generate the aromatic product and water. A catalyst for the overall Diels-Alder-dehydration reaction may participate in one or both of these steps.

One class of potential catalysts previously unreported were *pure Lewis acid molecular sieves*, specifically high-silica molecular sieves containing metal centers (Sn^{4+}, Ti^{4+}, Zr^{4+}) within the silica framework. These materials have been found to be useful in various Lewis acid-catalyzed processes, including isomerizations of carbohydrates[30,31] and the Meerwein-Ponndorf-Verley (MPV) reduction of carbonyl compounds.[32] Since homogeneous Lewis acids had already been shown to be effective for the Diels-Alder-dehydration between DMF and ethylene, it was reasoned that these solid Lewis acid microporous materials should also be useful. Furthermore, it was proposed that the Lewis acid molecular sieves would not only be effective catalysts for the reaction between DMF and ethylene, but may also be selective in Diels-Alder-dehydration reactions involving *oxygenated* furans, such as HMF or FDCA.[33]

The Diels-Alder-dehydration reaction conditions for using ethylene require high temperatures (150-300 ^{o}C) and pressures (30-70 bar) in the presence of an acid catalyst, and one main issue that was anticipated was the large number of side reactions and/or polymerizations that would be available to the oxygenated/functionalized furans at these conditions. Pure Lewis acidic molecular sieves were interesting potential catalysts for several reasons. First, Lewis acid molecular sieves may catalyze fewer side reactions than the Bronsted acid counterparts, H-Beta or H-Y zeolites, allowing for more selective catalysis for the Diels-Alder-dehydration reaction. Some side reactions that would be possible with HMF are dehydroxymethylation, etherification (by forming HMF dimers), and decarbonylation, and FDCA may undergo decarboxylation. Lewis acids were thought to be less effective than Bronsted acids in catalyzing some or all of these side reactions. Secondly, the microporous environment of the molecular sieve catalysts may prevent dimerizations/polymerizations of HMF from occuring due to spacial constraints at the acid site. Lastly, the micropores of the Lewis acid molecular sieves are hydrophobic (when synthesized in fluoride media) due to the low density of defect sites and nearly pure silica composition.[34] For reactions that produce water as a product, such as the Diels-Alder-dehydration reaction, the poisoning effect of water on Lewis acid catalysis is mitigated. The water is bound less strongly to the Lewis acid center in the hydrophobic, microporous environment and can be more easily displaced by an organic reactant molecule.[35] One interesting example of the exploitation of this property has been the use of these materials as Lewis acid catalysts for the isomerization of glucose to fructose in pure water solvent.[30]

1.5 Stategies for investigating novel Diels-Alder routes to PTA.

The investigation of new Diels-Alder routes to PTA from HMF and ethylene involved several strategies. First, the catalysis of a traditional Diels-Alder cycloaddition reaction between furan and acrylic acid using the proposed Lewis acid molecular sieves was studied (Chapter 3). The cycloaddition between furan and acrylic acid was successfully catalyzed by molecular sieves having the Beta topology containing Sn^{4+}, Zr^{4+}, and Ti^{4+} metal centers (Sn-Beta, Zr-Beta, Ti-Beta). The results show that these solid Lewis acids, under the reaction conditions used for this system (50^{o}C), successfully catalyze the cycloaddition but not the dehydrative aromatization of the Diels-Alder adduct to the substituted aromatic product (benzoic acid). The formation of benzoic acid was instead achieved by using a strong Bronsted acid (sulfuric acid). This work showed that the Lewis acid Beta molecular sieves can behave as selective Diels-Alder catalysts and further suggested their potential usefulness in Diels-Alder-dehydration reactions between oxygenated furans and ethylene.

Next, new Diels-Alder-dehydration reaction systems were explored using either (1) HMF with ethylene to produce the PTA intermediate 4-(hydroxymethyl)benzaldehyde (HMB), or (2) a protected derivative of HMF to react with ethylene to produce the PTA intermediate (Chapter 4). HMF may be protected through a variety of ways, such as converting the hydroxymethyl functionality to an alkoxymethyl group through etherification with alcohols or converting the aldehyde functionality to an acetal by reaction with diols or alcohols. During these reaction screening studies, the Lewis acid molecular sieves were applied mostly as possible catalysts.

The third approach to developing a pathway to PTA from HMF was to simply improve the yields of PTA from the Diels-Alder-dehydration reaction between FDCA and ethylene (Chapter 4). If the rate of PTA production from FDCA could be significantly improved, either by applying a catalyst or finding new reaction conditions, this would allow for a breakthrough in producing bio-PTA. Here, the Lewis acid molecular sieves were again used mostly as potential catalysts. The main outcome was the successful use of the Lewis acid Beta molecular sieves in producing small amounts of PTA from FDCA in a reaction system using *dioxane solvent*. Although FDCA yields of up to only ~3% were achieved, the reaction product solutions were “clean” with little humins/coke formation and low conversion of the FDCA reactant to side products. Conversely, when Bronsted acid zeolites and homogeneous Lewis acids were used as catalysts, the product solution was “dark” from significant humins formation without any PTA being produced.

The final approach taken for developing a new ethylene Diels-Alder-dehydration pathway to PTA from HMF was to *partially* oxidize HMF to 5-(hydroxymethyl)-2-furoic acid (HMFA) before reacting with ethylene to produce the PTA precursor, 4-(hydroxymethyl)benzoic acid (HMBA). HMBA may then be subsequently oxidized to PTA. This reaction was achieved using Sn-Beta with 20-30% selectivity to HMBA.[36,37] When HMFA was protected using an alcohol (methanol) to produce the ether/ester form, methyl 5-(methyoxymethyl)furan-2-

carboxylate (MMFC), MMFC reacted with ethylene over Zr-Beta to form the product, methyl 4-(methoxymethyl)benzene carboxylate (MMBC), with >70% selectivity at >20% yields after 6 hours of reaction. Chapters 5, 6 and 7 will be devoted to discussing the findings of the new ethylene Diels-Alder-dehydration reactions involving HMFA and MMFC that allow for a new oxidation pathway to bio-PTA from HMF.

1.6 References

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