Oxygenated Commodity Chemicals from Chemo-Catalytic Conversion of Biomass Derived Heterocycles

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Introduction

Biomass is an abundant source of renewable carbon, which could form the basis for sustainable fuels and chemicals to replace those derived from fossil fuel resources.[1,2] During the past decade there have been multiple large projects focused on producing renewable fuels from biomass. These pioneer processes have often struggled to reach commercialization due to operational challenges, scale up challenges, and the low margins and high product volumes required for economic viability. The production of oxygenated chemicals from biomass offers several advantages compared to production of biofuels including: (1) chemicals are higher value, allowing for profitability at moderate scale (10–30 kton/yr) and sometimes even small scale (<1 kton/yr); (2) oxygenated chemicals require less deoxygenation, and therefore less hydrogen input and higher product mass yields compared to completely deoxygenated fuels; and, (3) target chemicals use the inherent functionalities (e.g., alcohols, cyclic ethers, C = C and C = O bonds, chiral centers) present in biomass. Bio-based chemicals can also be coproduced with biofuels thereby improving the economics of bio-refineries.[3–5] Synergies between bio-refineries and conventional refineries (e.g., utilizing hydrogen surplus for hydrogenation; integrating refinery waste heat) could further improve economic viability.

In recent years, several key oxygenated products from lignocellulosic biomass have been examined. These molecules can be divided into two classes: (1) chemicals that are identical to petroleum derived chemicals, and (2) new biomass derived chemicals that are not currently in the petrochemical infrastructure. The opportunity with this first route is that there is already a well-established market for these products. However, the challenge with this route is that it directly competes with the existing petroleum derived infrastructure, which is often at large scale where the chemicals are produced with depreciated assets. The opportunity with the new biomass derived chemicals is that these oxygenated molecules are difficult to produce from petroleum feedstocks and can have unique properties, with applications in areas including solvents, polymers, and surfactants. However, the market for these products is not established and it will take time for these products to gain market acceptability. The fully loaded production price of these new biomass derived chemicals could be comparable ($1000–5000/ton) to existing petroleum-derived commodity chemicals if they are produced on the large scale. These biomass-based chemicals can be produced from nonedible biomass. Rigorous life cycle assessment models have shown that biomass-based chemicals can have >60% (even 95%) lower carbon footprint than petroleum derived chemicals.[6–9] Products made from sustainable chemicals are appealing to end users that are increasingly concerned with issues regarding global warming and sustainability.
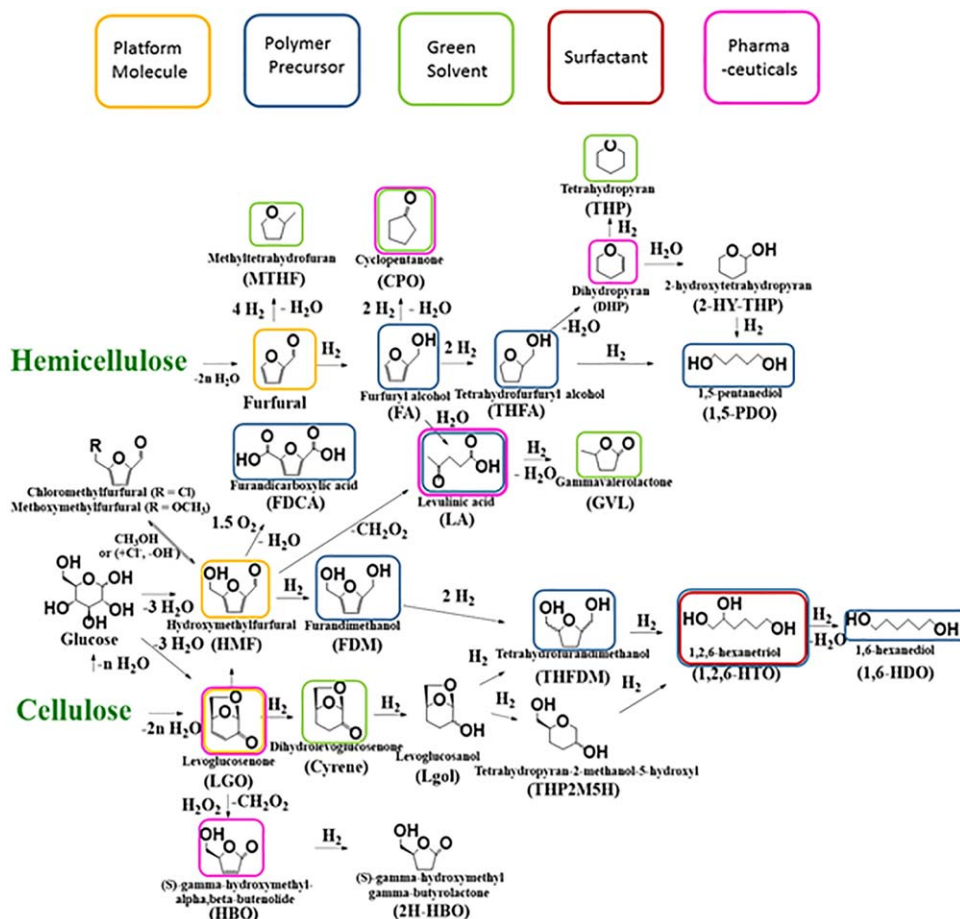
Scheme 1. Reaction network for conversion of biomass to high-value oxygenated chemicals. Proposed applications of different products are highlighted in different colors. Table 1 provides a summary of the physico-chemical properties of the molecules described.

Several recent studies have shown that different biomass heterocycles, including levoglucosenone (LGO), 5-hydroxymethylfurfural (HMF), and furfural, can be produced from biomass in high yields and at low costs ($1000–$5000/ton) if produced at scale (>10 kton/yr).[10–12] Scheme 1 shows the reaction chemistry of converting biomass-derived heterocycles to different oxygenated products with potential applications highlighted. Table 1 shows relevant physico-chemical properties of these molecules. LGO and/or HMF can be produced (depending on the reaction conditions) from dehydration of cellulose, glucose, or other carbohydrates in up to 50–60% yield.[11,23–26] These molecules can then undergo selective hydrogenation over metal catalysts, as well as selective hydrogenolysis/dehydration over metal-acid catalysts, to produce a variety of reduced oxygenated products.[27–29] These products include α,ω-diols such as tetrahydrofurandimethanol (THFDM) and 1,6-hexanediol (1,6-HDO), polyols such as 1,2,6-hexanetriol (1,2,6-HT), and renewable solvents such as dihydrolevoglucosenone (Cyrene).[21,30] Alternatively, HMF can be selectively oxidized to the polymer precursor furandicarboxylic acid (FDCA).[31] Furfural is produced from dehydration of hemicellulose or C_5 sugars in up to 95% yield.[12] Similar to the C_6 route, furfural can undergo successive hydrogenation and/or hydrogenolysis reactions to produce polymer precursors furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), and 1,5-pentanediol (1,5-PDO),[32,33] as well as renewable solvents including 2-methyl-tetrahydrofuran (MTHF), cyclopentanone (CPO), and tetrahydropyran (THP).[34,35] The renewable solvent γ-valerolactone (GVL) can be synthesized either from hydration of FA (C_5 pathway) or ring-opening of HMF (C_6 pathway, with loss of formic acid).[36,37] Lignin, which constitutes approximately 20 wt % of lignocellulose, is generally burnt for process heat and power in the majority of techno-economic analyses of biomass conversion; lignin conversion into valuable products remains challenging but is an ongoing area of research.[38–40] We note that while we have highlighted LGO, HMF, and furfural as attractive platform molecules for the production of high-value oxygenated chemicals, Scheme 1 is not meant to be an exhaustive list of chemicals produced from chemo-catalytic biomass conversion.

1,6-HDO is an example of an oxygenated commodity chemical currently produced from petroleum but which is an attractive target for production from biomass because of its high cost and volume. Two companies (Rennovia Inc.[8] and DuPont[41]) have submitted patent applications on technology to produce 1,6-HDO from biomass. 1,6-HDO is used as a feedstock to make polyester polyols and has a market price of $3000–4500/ton and volume of nearly 150 kton/yr.[42] The petrochemical route for 1,6-HDO production from benzene involves five reaction steps as shown in Scheme 2.[43,44] Benzene is hydrogenated to cyclohexane over a metal catalyst and then oxidized to a mixture of cyclohexanol and cyclohexanone

Table 1. Physico-Chemical Properties of Molecules in Scheme 1

Molecule	Abbreviation	Formula	MW (g/mol)	Functionalities	b.p (°C)	m.p (°C)	Viscosity (cps), 25°C	Solubility in Water (g/L)	Dielectric constant
Levoglucosenone[13]	LGO	$C_6H_6O_3$	126.1	Ketone, C=C bond, chiral	256				
Furfural[14]		$C_5H_4O_2$	96.1	Aldehyde, furan	162	−37	1.49	83	41.9
5-Hydroxymethylfurfural[13,15]	HMF	$C_6H_6O_3$	126.1	Aldehyde, alcohol, furan	291	32			
2-Methyltetrahydrofuran[16]	MTHF	$C_5H_{10}O$	86.1	Cyclic ether	80	−136	.46	35	7.0
Cyclopentanone[17]	CPO	C_5H_8O	84.1	ketone	130	−51	1.07	29	
Tetrahydropyran[13,18,19]	THP	$C_5H_{10}O$	86.1	Cyclic ether	88	−45	0.80	8.6	5.7
Tetrahydrofurfuryl alcohol[17]	THFA	$C_5H_{10}O_2$	102.1	Hydroxy methyl ether	178	<-80	6.2	miscible	13.6
Levulinic acid[13,20]	LA	$C_5H_8O_3$	116.1	Keto acid	246	33		675	
Gamma-valerolactone[13]	GVL	$C_5H_8O_2$	100.1	Lactone	207	−31		miscible	
Dihydrolevoglucosenone[21]	Cyrene	$C_6H_8O_3$	128.1	Ketone, chiral	203	−20	11.0	miscible	∼3.4
1,5-pentanediol[13]	1,5-PDO	$C_5H_{12}O_2$	104.2	α,ω- diol	239	−18		miscible	
1,6-hexanediol[13,22]	1,6-HDO	$C_6H_{14}O_2$	118.2	α,ω-diol	250	43		500	
Furfuryl alcohol[17]	FA	$C_5H_6O_2$	98.1	Hydroxymethyl ether, furan	170	−29	4.6	miscible	
2,5-furandimethanol[13,15]	FDM	$C_6H_8O_3$	128.2	α,ω-diol	275	75			
2,5-tetrahydrofurandimethanol[13]	THFDM	$C_6H_{12}O_3$	132.2	α,ω-diol, cis/trans	265	< −50			
2,5-furandicarboxylic acid[13,15]	FDCA	$C_6H_4O_5$	156.1	α,ω di-acid, furan	420	300		1	
1,2,6-hexanetriol[13,15]	1,2,6-HT	$C_6H_{14}O_3$	134.2	Polyol		−20	2630	miscible	
3,4-dihydropyran[13]	DHP	C_5H_8O	84.1	C=C bond, cyclic ether	86	−70			
(S)-gamma-hydroxymethyl-alpha, beta butenolide	HBO	$C_5H_6O_3$	114	butenolide, chiral					
(S)-gamma-hydroxymethyl-alpha, beta butyrolactone	2H-HBO	$C_5H_8O_3$	116	Lactone, chiral					

("KA Oil") over a homogeneous cobalt catalyst. The conversion must be kept low (5–7%) in this process as cyclohexanone and cyclohexanol undergo undesired over-oxidation reactions. This step has a high separation and recycle requirement for the unreacted cyclohexane. There is also a safety hazard of combustion of the hydrocarbon reagent. The KA oil is then oxidized to adipic acid using concentrated nitric acid (a corrosive reagent) which also releases N_2O in the process. N_2O is a harmful gas which requires additional treatment to avoid its release. Adipic acid is then hydrogenated in methanol solvent via the intermediate dimethyl adipate. In contrast, the envisaged biomass-derived route would involve selective hydrodeoxygenation of an oxygenated feedstock (Scheme 1) rather than reduction and oxidation of a hydrocarbon feedstock, and could potentially be operated at high yield, with fewer reaction steps, avoiding toxic reagents. Biomass-derived routes to 1,6-HDO also have a lower CO_2 footprint than production from petroleum.[8]

This Perspective article discusses new chemical catalytic approaches to convert biomass-derived platform molecules (LGO, HMF, and furfural) to renewable chemicals. First, we highlight recent literature in this area including catalytic reaction networks and product applications. We then examine an example of producing polyesters from biomass-derived diols and di-acids, an area of current research in academia as well as in industry. Finally, we comment on strategies to promote the adoption of new renewable chemicals produced from biomass. The price of oxygenated commodity chemicals from biomass is often prohibitively high for wide-scale industrial use at the current small scale of production. The production cost of these molecules decreases with the scale that they are produced, similar to all commodity chemicals. While many of these biomass-derived molecules could potentially be drop-in replacement petroleum-derived products or could have unique and desirable properties, there is uncertainty in their potential applications. Scale-up risk and the capital intensity of pioneer technologies, lead to a chicken-and-egg problem about who is willing to accept the risk involved in developing new technologies, even if the end result could be a greener, more efficient, and profitable process. Addressing this problem requires
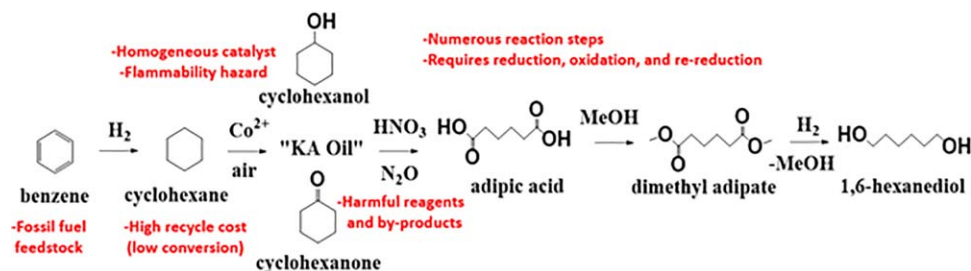
Scheme 2. Reaction network for current production of 1,6-hexanediol from petroleum-derived benzene. Undesirable aspects of this process are indicated in red.

collaboration throughout the value chain between producers, formulators, brand owners, and even the final consumers of these molecules. Testing the properties of new biomass-derived products in their proposed applications and assessing the industrial feasibility of proposed new technologies will be imperative to the success of oxygenated commodity chemicals from biomass. While this article focuses on chemo-catalytic conversion of biomass, the insights regarding the economics and scale-up of new technologies discussed in this article are relevant for biochemical conversion strategies as well. Efforts are also underway to integrate bio-catalytic and chemo-catalytic approaches to produce high-value chemicals from biomass, as discussed in a recent review.[45]

Products from C_6 (LGO and HMF)

Levoglucosenone

LGO is a versatile chiral molecule which was discovered as a biomass pyrolysis product in the 1970s.[46] LGO has two cyclic ether groups, two chiral centers, and a C = C double bond conjugated with a ketone. It has recently gained commercial interest due to the maturation of the Furacell[TM] technology, a continuous process to convert a wide range of cellulosic biomass into LGO.[47] This technology was developed by the Australian company Circa and is, as of 2017, being operated at a pilot plant producing 50 ton/yr LGO (in partnership with the multinational Norske Skog). LGO can also be produced from cellulose in polar aprotic solvents.[15] While LGO currently has a high market price (>$10,000/ton) due to its small scale of production, process models have indicated that it could be produced at prices of $3500/ton if LGO is produced at scales of >30 kton/yr (the techno-economic analysis was performed using pure cellulose of a feedstock).[11]

Partial hydrogenation of LGO produces Cyrene over a metal catalyst in a solvent free process.[21] Cyrene is attractive as a renewable, non-toxic polar aprotic solvent which displays similar solvent properties to N-methylpyrrolidone (NMP), dimethylformamide (DMF), and dimethylacetamide (DMAC).[21] NMP, DMF, and DMAC are under growing worldwide regulatory pressure due to their toxicity. In contrast, the EU has recently certified Cyrene as a nontoxic solvent.[46] While it remains to be seen whether Cyrene is a viable replacement for other industrial solvents, the overall market for pharmaceutical and specialty solvents represents 900 kton/yr and is growing at 4%/yr.[48] Cyrene has been evaluated successfully as a solvent in a wide range of applications, including fluorination,[21] C-C bond formation (e.g., Menschutkin reaction,[21] Sonogashira cross-coupling, and Cacchi-type annulations[49]), urea synthesis,[50] and MOF synthesis.[51] Cyrene has also been demonstrated as a solvent for nanomaterials synthesis, for example in delaminating graphite into graphene, which was independently reported by Salavagione et al.[52] and Gharib et al.[53]

LGO can also be converted into (S)-γ-hydroxymethyl- α,β-butenolide (HBO) and (S)-γ-hydroxymethyl-γ-butyrolactone (2H-HBO) involving a lipase-mediated Baeyer–Villiger oxidation and an acid hydrolysis step.[54,55] HBO finds application in the synthesis of a range of pharmaceuticals (e.g. Burseran and Isostegane) while 2H-HBO is an intermediate to C_{7-12} 5-alk(en)yl-γ-lactones,[54] which is known as Laiscent[TM], a dairy flavor. LGO is a promising precursor for pharmaceuticals,

with many applications having been reported in the 1980s–1990s,[56] and with more recent examples being synthetic routes to the antiviral indinavir and a range of pharmaceutically active cyclopropylesters.[57,58]

LGO or Cyrene can be quantitatively hydrogenated to threo- and erythro-Lgol over supported metal catalysts.[59] Lgol is a key intermediate in the production of downstream hydrogenolysis products. The stereoisomer ratio of Lgol can be tuned by changing the catalyst properties. We have recently shown that Lgol can be ring-opened and hydrogenated to THFDM (60% selectivity) and tetrahydropyran-2-methanol-5-hydroxyl (THP2M5H; 20% selectivity) in THF solvent using a Pd/SiO_2-Al_2O_3 catalyst. THFDM is an α,ω-diol which may have similar applications to existing α,ω-diols such as 1,6-hexanediol; alternatively, both THFDM and THP2M5H can be further converted to 1,6-hexanediol by hydrogenolysis. Lgol conversion to THFDM over Pd/SiO_2-Al_2O_3 produces a THFDM cis/trans ratio of 2.6, while in contrast, HMF hydrogenation produces predominantly the cis- isomer of THFDM.[59] The ability to alter the cis/trans ratio offers the potential to control polymer tacticity, which can influence polymer properties.[60]

Hydroxymethylfurfural

HMF is another biomass platform molecule which can be produced from dehydration of cellulose or C_6 sugars. The current price of HMF is high (>$10,000/ton) but several companies are working on producing HMF at larger scale which would decrease the HMF price. Techno-economic modeling of HMF production in the literature predicts costs of $1000/ton in large scale processes (60 kton/yr), largely using fructose as a feedstock.[61,62] Several articles have discussed approaches to produce HMF.[14,17,63–65] Control over the solvent allows the dehydration selectivity to be tuned between LGO (minimal water content) and HMF (higher water content).[13,15] LGO can also be isomerized to HMF under aqueous acidic conditions,[66,67] with a maximum yield of 65%.[67] Using HCl as an acid catalyst, the chlorinated form of HMF, chloromethylfurfural (CMF), can be produced in up to 75% yield from cellulose due to its higher stability than HMF.[68,69] HMF can be partially hydrogenated into furandimethanol (FDM), or fully hydrogenated into THFDM quantitatively over a metal catalyst.[70] As discussed above, the α,ω-diol functionalities in FDM and THFDM make them possible substitutes for 1,6-hexanediol.[71]

Further acid-catalyzed conversion of HMF results in levulinic acid, a C_5 product (with loss of formic acid) used in plasticizers, pharmaceuticals, and cosmetics.[72,73] Levulinic acid can also be produced from hydration of furfuryl alcohol. The market for levulinic acid, a derivative of HMF, is projected to reach USD $32.5 Million by 2021, at a CAGR (compound annual growth rate) of 14.0% between 2016 and 2021.[74]

Avantium's process to produce FDCA from fructose-derived HMF is one example of a bio-derived product undergoing commercialization.[75] Fructose is dehydrated in methanol solvent to methoxymethylfurfural (MMF), the methylated analogue of HMF. MMF is then oxidized to FDCA using a homogeneous catalyst, in a process similar to the oxidation of p-xylene to terephthalic acid. FDCA can be coupled with mono-ethylene glycol to form polyethylene furanoate (PEF), a green replacement for polyethylene terephthalate (PET), which is currently in the

process of being scaled up to a 50 kton/yr plant.[76] Recent work has shown that FDCA can be produced in high yield from fructose via acid-catalyzed dehydration to HMF followed by oxidation to FDCA over a heterogeneous Pt/C catalyst, avoiding use of a homogeneous base.[31] The product FDCA can be purified from the GVL-water system by crystallization, and recycled FDCA can be used as an acid catalyst in the dehydration step, avoiding use of a corrosive acid.

DuPont and Archer Daniels Midland are collaborating on a project to produce furan dicarboxylic methyl ester (FDME), a derivative of FDCA, from fructose.[77] FDME can be converted into polymers such as the 100% bio-based polyester polytrimethylene furandicarboxylate (PTF), using renewable 1,3-propanediol as the comonomer. PTF has also shown promise as a polymer for use in the beverage packing industry with improved shelf life.

Tetrahydrofurandimethanol (via LGO or HMF)

THFDM can be produced from hydrogenation of either HMF or LGO (Scheme 1). THFDM can be further converted to either 1,2,6-hexanetriol (1,2,6-HTO) or 1,6-hexanediol (1,6-HDO) over Pt-WO$_x$/TiO$_2$.[27,78] 1,2,6-HTO has numerous applications as a surfactant,[79,80] low-toxicity solvent for increasing viscosity in cosmetics and pharmaceuticals, and humectant.[81] Derivatives of 1,2,6-hexanetriol can be used in hydraulic fluids and as corrosion inhibitors.[82] The trifunctionality of 1,2,6-hexanetriol can be used to for crosslinking in polyesters and alkyd resins.[83] Esters of 1,2,6-hexanetriol with longer-chain carboxylic acids are useful plasticizers for PVC and cellulose acetate, as well as for rubber polymers, such as nitrile rubber (NBR) and neoprene.[81]

1,2,6-HTO can be further hydrodeoxygenated into 1,6-HDO with a selectivity above 90% over Pt-WO$_x$/TiO$_2$.[30] These renewable routes to 1,6-HDO from LGO or HMF are attractive candidates to replace the petroleum-derived route from benzene (Scheme 2). Rennovia has recently built a pilot plant for bio-based 1,6-HDO and claims a much better profit margin than petroleum-based 1,6-HDO.[8] DuPont has reported that LGO can be converted to 1,6-hexanediol by a two-step process that involves LGO conversion into THFDM in up to 84% yield over a Pt/C catalyst, and followed by THFDM conversion into 1,6-hexanediol in 83% yield over a PtW/TiO$_2$ catalyst, resulting in an overall 1,6-HDO yield of 70% from LGO.[41] Our group has studied the catalytic chemistry for production of 1,6-HDO from THFDM over Pt-WO$_x$/TiO$_2$ catalysts.[78] Hydrogen spills over from Pt sites onto WO$_x$/TiO$_2$ to reduce the W = O functional group and create Brønsted acid sites. This interaction between Pt and reduced WO$_x$ plays an important role in THFDM conversion.

Products from C$_5$ (Furfural)

Furfural is one of the most common biomass derived chemical intermediates with over 440 kton/yr of capacity available.[84] From 2006 to 2016 the cost of furfural has been between $800–1600/ton. The furfural price increased to $2700/ton at the end of 2017 due to environmental regulations enforced on China's furfural production industry. IHS (Information Handling Services) claims that the cost of furfural in the coming years will be in the $1000–1100/ton range thus making it a low cost and abundant biomass-based building

block. Furfural is produced via acid-catalyzed dehydration of biomass-derived xylose (or hemicellulose) in up to 95% yield.[12] Currently, China, South Africa, and the Dominican Republic are the major producers of furfural and its derivatives.

While furfural can be utilized directly as a solvent or in the production of synthetic resins,[14] it can also be used to produce higher-value molecules which fit into larger markets (Scheme 1).[85] Furfural can be partially hydrogenated to furfuryl alcohol (FA) or undergo total hydrogenation to tetrahydrofurfuryl alcohol (THFA).[28] The largest application segment for FA is the manufacture of foundry resins which accounts for over 80% of overall furfural market. THFA is a biodegradable specialty solvent used in agricultural applications, printing inks, and cleaning products.[86] In recent years, the global THFA consumption is over 85 kton/yr with a market price of $3,000/ton.

FA and THFA can undergo ring-opening reactions to produce the α,ω-diol, 1,5-pentanediol (1,5-PDO). While 1,5-PDO has been produced by direct hydrogenolysis of THFA over bimetallic catalysts such as RhRe,[32,87] a three-step pathway consisting of dehydration of THFA to 3,4-dihydropyran (DHP), hydration of DHP to 2-hydroxytetrahydropyran (2-HY-THP), and conversion of 2-HY-THP to 1,5-PDO has been shown to be an economically advantageous method of 1,5-PDO production and results in improved 1,5-PDO yields (∼87%).[33,88] The intermediate DHP is produced in high yields (90%) in the first step of this pathway via the gas-phase dehydration of tetrahydrofurfuryl alcohol over γ-Al$_2$O$_3$.[33,89] The C = C bond in DHP enables other functionalities to be added at the α position relative to the ether oxygen. This chemistry is useful in synthesizing agrochemicals[90] and pharmaceuticals.[91] Alternatively, DHP can be hydrogenated to tetrahydropyran (THP) in the liquid phase over metal catalysts in nearly 100% yields.[92]

The renewable solvent, 2-methyltetrahydrofuran (MTHF), can also be made in a single step from furfural via a methyl furan intermediate.[35] Furfural-derived cyclic ethers such as MTHF and THP could potentially be used to replace petroleum-derived polar aprotic solvents such as tetrahydrofuran (THF) and 1,4-dioxane. In fact, MTHF has many benefits to THF as a solvent including immiscibility with water, lower volatile organic compound (VOC) emissions, and improved results in a variety of applications, particularly in the pharmaceutical industry.[16,93] Furthermore, a life cycle analysis of the production of MTHF from furfural showed a 97% reduction in emissions compared to the current industrial route to make THF.[94] THP also shows potential as a green alternative to THF or 1,4-dioxane, having similar properties with the exception of its limited solubility in water, which could be advantageous in liquid-liquid separation processes.[19]

Another chemical derived from furfural is cyclopentanone (CP). Hronec et al. reported the synthesis of CP via the aqueous-phase ring-rearrangement of furfural in hydrogen atmosphere over supported metal catalysts.[34] CP has applications as a solvent and in the synthesis of specialty chemicals, including pharmaceuticals, agrochemicals, rubbers, and flavors.[95]

Gamma valerolactone (GVL), produced via hydrogenation of levulinic acid[37] derived from either furfural[36] or HMF, can be used as a solvent in the production of various chemicals from biomass.[96,97] One example is in the deconstruction of lignocellulosic biomass into lignin and C$_5$/C$_6$ sugars using a
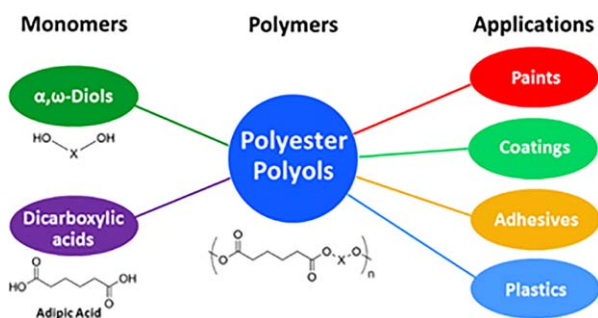
Figure 1. Schematic of polyester polyols end-use applications and production from α,ω-diols and adipic acid.

GVL-water solvent mixture and dilute sulfuric acid.[56] Here, the polar aprotic GVL resulted in much higher yields than polar protic ethanol, and the high boiling point of GVL was leveraged in order successfully distill the furfural product.[98]

Example: Biomass Based Polyesters

Much of the polymer industry is built on the "α, ω" functionality (e.g., di-acids, diols) which allows for symmetric reactions at the terminal ends of the molecule. As shown in Scheme 1, there are several products from biomass which possess these functionalities and which could be used to produce polymers such as polyester polyols. Global demand for polyester polyols stood at 2600 kton/yr valued at $5.6 billion in 2015 with a CAGR of 5.3%.[12,99] Polyester polyols are used in four major applications: (1) cast elastomers, (2) thermoplastic urethanes (TPU), (3) polyurethane coatings, and (4) adhesive and sealants.[100]

Polyester polyols are synthesized via co-polymerization of C_2-C_6 α,ω-diols with dicarboxylic acids (primarily adipic or terephthalic acid (TPA)) (Figure 1). Polyester polyol properties can be tuned by varying the diol chain length or the di-acid functionality: for example, adipic acid for an aliphatic backbone or TPA for an aromatic backbone. The choice of the monomers to use for polyester polyols depends on both the desired properties as well as monomer costs. A study of the properties of polyester polyols made with adipic acid and α,ω-diols of varying chain length was performed by DuPont as shown in Table 2.[100] The resulting polyester polyols have many similar properties (MG, OH number, viscosity) but also exhibit some properties that make biomass-derived diols

unique, such as the odd-even effect on melting point.[100] The current worldwide consumption of 1,5-PDO is about 3 kton/yr but at a high price of $6000/ton due in part to limited readily accessible C_5 petrochemical feedstocks. 1,4-butanediol and 1,6-HDO have larger market sizes of 3200 kton/yr (average price $2270/ton) and 150 kton/yr (average price $3450/ton), respectively.[5,88] Polyesters can also be produced from polycondensation reactions of glycerol (a by-product of biodiesel production) and adipic acid.[101]

DuPont's study of polyester polyol properties also highlights their new technology to produce 100% biologically-derived 1,3-propanediol (1,3-PrDO). While this Perspective article deals predominantly with chemical catalytic conversion of bio-derived molecules, the biological production of 1,3-PrDO by fermentation constitutes a successful example of an industrial scale fermentation process which outperforms the alternative petrochemical route.[102] This technology was developed and successfully commercialized by DuPont and Tate & Lyle and is known under the trademark Susterra®.[100] 1,3-PrDO is prepared by fermented from corn sugar, a rapidly growing renewable feedstock, to meet the demand of the DuPont Sorona® polymer polytrimethylene terephthalate (PTT). Susterra® 1,3-PrDO also can substitute into some of the applications of 1,4-BDO, such as polyurethane coatings, adhesives, sealants, and elastomers (CASE), as well as in thermoplastic polyurethanes (TPU), with some variation in the resulting polymer properties (e.g., low thermal transition temperature).

Another example of biomass-derived polyesters is the substitution of PET with bio-derived PEF. This is based on the structural resemblance between TPA and FDCA. Corbion has developed a proprietary biocatalytic process to FDCA[103] while the BASF-Avantium joint venture "Synvina" is commercializing Avantium's YXY technology.[75] This process consists of two steps: (1) the catalytic dehydration of a carbohydrate feedstock in an alcohol yielding alkoxymethyl-furfural (RMF) and alkyl levulinates; (2) the catalytic oxidation of RMF in acetic acid to FDCA. PEF is obtained by the esterification of FDCA with ethylene glycol (EG). FDCA and TPA are sufficiently similar to allow the use of existing PET polymerization plants to convert FDCA to PEF without major changes in infrastructure. The Coca-Cola Company, Danone and ALPLA are working in a collaboration with Avantium to further develop and commercialize PEF bottles to the market.[75] PEF bottles have been proven to outperform PET bottles in many areas, including withstanding gas permeability, high glass transition

Table 2. Properties of Polyester Polyols Synthesized from Adipic Acid and α,ω-diols of Varying Chain Length (Data Obtained from *DuPont Tate & Lyle BioProducts*[100])

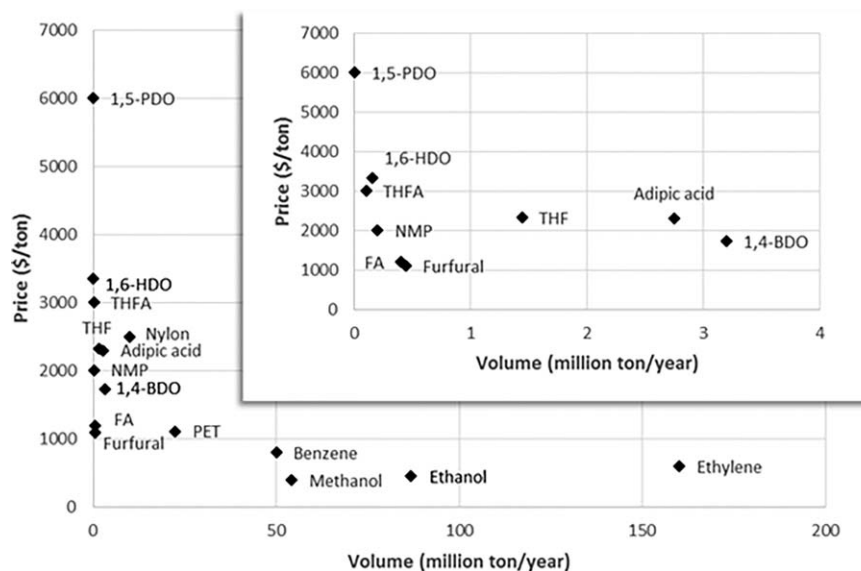| Molecule	MW (g/mol)	OH Number (mg KOH/g)	Acid Number	Viscosity (cP)	Glass Transition (°C)	Melting Point (°C)
1,2-ethanediol (ethylene glycol; EG)	2114	52.8	0.53	1334	−46.9	48
1,3-propanediol (1,3-PrDO)	2029	55.3	0.36	1471	−59.7	39.7
1,4-butanediol (1,4-BDO)	2110	53.2	0.61	1482	−53.7	53.3
1,5-pentanediol (1,5-PDO)	2188	51.3	1.24	1316	−61.8	38.6
1,6-hexanediol (1,6-HDO)	1961	57.3	0.26	1100	none	51.8

Figure 2. Current market price and market size of selected commodity chemicals (based on 2016 market conditions). References provided: Furfural[84]; FA[107]; THFA[107]; 1,5-PDO[88]; 1,6-HDO[108]; NMP[109]; 1,4-butanediol[110]; THF[111]; adipic acid[112]; nylon[113]; PET[114,115]; ethanol[116]; benzene[117]; methanol[118]; ethylene.[119]

temperature, and low melting temperature. The estimated market potential for FDCA is expected to reach $500 million (∼$1100/ton) by 2020, growing at an exponential CAGR of 367% from 2014 to 2020, owing to the projected commercial production using bio feedstock.[104] In addition to the polyester PEF, FDCA can also be processed to polyamides, polyurethanes (e.g., foams, coatings) and esters (e.g., personal care products and lubricants).

Towards Bulk Production of Biomass Derived Chemicals—Economics and Scale-Up of New Technologies

While the field of catalytic biomass conversion to chemicals has made major technological advancements in the past years, industrial adoption remains limited. This limitation is due in part to a "chicken-and-egg" problem as well as the long time-frame required for new technologies to be implemented in the chemical industry. In some cases, these new technologies are not only greener, but also potentially more efficient and more profitable than the current petroleum-derived routes. However, because these molecules are currently produced at small scale and at high cost, end-users in the solvents, polymers, surfactants, and other industries are unwilling to adopt these new technologies, or even fully study the potential of these molecules to replace those derived from petroleum. The prices of renewable chemicals such as LGO and HMF remain prohibitively high (>$10,000/ton), due in part to their small scale of production often in batch processes.

Techno-economic analyses have shown that biomass-derived commodity chemicals could be produced at lower costs ($1000–5000/ton) if produced at larger scales (>10 kton/yr) in continuous flow processes. In general, the unit cost of chemical facilities is reduced by increasing the size of the facility and moving from batch to continuous operation. A recent analysis has shown that the capital costs for existing commercial

bio-refineries scale with the plant size with exponents ranging from 0.6 to 0.9 depending on the type of technology.[105] Once facility costs are determined, direct and indirect overhead cost factors (e.g., installation costs and project contingency) are applied to determine a feasibility-level estimate of total capital investment, which along with the plant operating expenses (developed based on mass and energy balances) is used in a "discounted cash flow rate of return" analysis to determine plant gate price of the product for a given discount rate. The plant gate price is also called the minimum selling price (MSP), required to obtain a net present value (NPV) of zero in 20–30 years for a given internal rate of return (IRR) after taxes. It is reasonable to expect a steady decrease in MSP as the plant size increases within a certain range. The plant size must also be selected based on market and techno-economic analysis to mitigate the risk associated with feedstock supply chain, product market volume, and initial investment scale. Accurately estimating the market size and hence the MSP price of a new proposed chemical is challenging as it requires a detailed knowledge of the market. Techno-economic analysis for new technologies should use pioneer plant analysis (rather than nth plant analysis), to account for risk in unproven technologies.[106] A high IRR (>30%) is often preferred for industrial interest in new technologies.

If a biomass-derived oxygenated chemical is to be a drop-in replacement for an existing commodity chemical, it should have a lower production cost than the existing chemical at the current market price. Figure 2 shows the current market price for selected commodity chemicals, including products which could potentially be replaced by biomass-derived oxygenates from Scheme 1. Renewable routes to 1,6-HDO can only be economically competitive if their production cost is less than the current market price of $3,340/ton for 1,6-HDO, unless consumers are willing to pay a higher price for a more sustainable version of 1,6-HDO based products. PET, which could potentially be replaced by HMF-derived PEF, has a price of
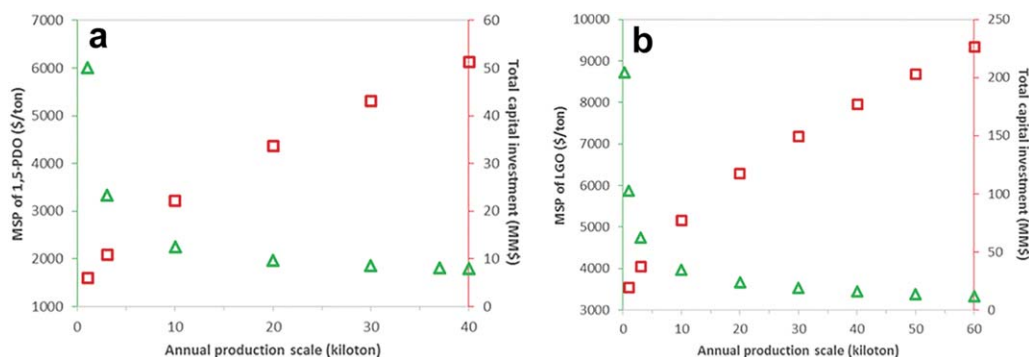
Figure 3. MSP and total capital investment as a function of plant size (annual production scale) (A) 1,5-PDO production from furfural via dehydration-hydration-hydrogenation pathway[88] (B) LGO production from cellulose in THF-water solvent.[11] Red squares: total capital investment. Green triangles: minimum selling price.

approximately $1000/ton (Figure 2). NMP, which could potentially be replaced by Cyrene, has a price of approximately $2000/ton. In addition to the market prices shown in Figure 2, efficient carbon utilization of the biomass feedstock is an important consideration in the selection of target products from biomass.

Based on the economic models for the production of 1,5-PDO from biomass-derived furfural[88] (Figure 3A) as well as the production of LGO from cellulose in THF solvent using sulfuric acid (Figure 3B),[11] the MSP and total capital investment are given as a function of annual production scale. For example, an increase of 1,5-PDO production from 1 kton/yr to 20 kton/yr would require additional $30,000,000 investment but would reduce the MSP of 1,5-PDO from $6000/ton to $2000/ton. As shown in Figure 1 1,5-PDO and LGO can indeed be cost-competitive with petroleum-derived oxygenated commodity chemicals, but only if they are produced at sufficiently large scale. Techno-economic analyses for the proposed FDCA production process from fructose indicate a MSP of $1350/ton for a plant size of over 100 kton/yr and a fructose feedstock price of $590/ton.[31] This price is slightly higher than the current price of PET ($1100/ton), indicating that PEF cannot compete with PET purely on a cost basis but could benefit from its advantageous properties. Based on private discussions with Circa, economic modeling suggests that the Cyrene production plant will be profitable at 5–10 kton/yr plant output, with selling prices below $10,000/ton. Cyrene has the benefit of being non-toxic compared to toxic NMP, potentially allowing for Cyrene to have a premium in price compared to NMP.[21,46]

Due to the wide variety of chemicals that can be produced from biomass (including drop-in products and new molecules) as well as the number of process technologies involved, techno-economic modeling of biomass conversion processes presents a complex problem. Process systems engineering approaches are thus required to address new challenges (e.g., diversity of biomass feedstocks; reliable property and cost models; systems tools to tackle novel process alternatives), thereby allowing us to systematically identify viable bio-refinery strategies in competition with petrochemical processes.[120–125] The design of the biomass supply chain should also be optimized taking into account geographically distributed feedstock availability, available transportation modes and associated costs, candidate plant locations, and demand

patterns.[126–129] We note that biomass feedstock availability is less of a concern when high-value chemicals are produced, as compared to fuels, because of the smaller product volumes and therefore smaller bio-refinery capacity required.

It often takes over 10 years to implement a new technology in the chemical industry. One example of a new technology in this field that has been developed is the production of polylactic acid from corn starch by NatureWorks.[130] NatureWorks started working on this technology in 1989. Five years later they had a semi-works plant with a capacity of 4 kton/yr. In 2002 they built a 88 kton/yr facility. Scale-up of a new technology requires a major capital investment. The question of which party in the supply chain (producers of these molecules, polymer manufacturers, formulators, or end-users) is willing to adopt the risk to develop these new technologies remains a major roadblock to industrial adoption. Collaboration between potential producers and users of these biomass-derived molecules is critical to overcoming this problem. In spite of the challenges with implementing these new technologies, the numerous societal benefits of these technologies should be kept in mind. These benefits include: (1) providing long term value and creating manufacturing jobs in rural communities, (2) lowering the carbon footprint of materials, and (3) reducing the dependence on nonrenewable fossil fuels as feedstocks for the chemical industry. The chemical industry is one of the few industries that can create long-term wealth by converting low value products into materials that society needs to maintain our standard of living. It is critical that our field continues to use our knowledge of chemical engineering to create new chemicals and materials from renewable biomass sources.

Conclusions

The biomass-derived molecules shown in Scheme 1 provide opportunities for sustainable new products often with unique properties that can be used in the polymer, solvent and surfactant industries. The processes for producing these compounds have potential advantages including using oxygenated functionalities present in biomass, avoiding the use of harmful reagents, and in some cases offering a high yield route demonstrated in continuous flow reactors over stable heterogeneous catalysts. These oxygenates include molecules currently produced from petroleum (e.g., 1,6-HDO) with a known market, as well as "new" molecules (e.g., FDCA, Cyrene and

THFDM) which have some uncertainty in the market and applications. The current market price of the majority of these chemicals is high (> $10,000/ton) because they are currently only produced in small-scale batch processes. The cost of these molecules could be brought down to $1000–$5000/ton if they are produced at larger scale (>10 kton/yr). There is a chicken-and-egg problem with development of these new technologies, as major capital investment in a new technology is inherently risky, while end-users will not adopt these new products unless they are already produced at economical scale and their properties can be tested. Therefore, the properties of end-products made from these molecules are often unknown. Materials made from these chemicals could have similar properties to petroleum-derived products, or could even have unique properties with added benefits compared to petroleum-derived products.

Some biomass-derived molecules, such as the renewable polar aprotic solvent Cyrene and the polymer precursor FDCA, are currently undergoing commercialization. Their success is partly due to the fact that these molecules have undergone extensive property testing showing that products made from these chemicals have distinct advantages over existing petroleum-derived products. Cyrene has been shown to be a non-toxic solvent, which can replace toxic solvents such as NMP and DMF for a variety of applications in organic chemistry. FDCA-derived PEF was shown to have improved barrier properties compared to petroleum-derived PET for use in plastic bottles. Similarly, DuPont's test of polyester polyols produced from linear α,ω-diols of varying chain length showed that biomass-derived 1,3-PrDO and 1,5-PDO had similar properties to diols traditionally derived from petroleum, including 1,4-BDO and 1,6-HDO, suggesting the potential for substitution while also offering the ability to tune polymer properties. Successfully demonstrating the applications of new biomass-derived products in their proposed applications decreases the risk involved in adopting these technologies. It is critical that scientists, engineers, and business leaders continue to focus on the long-term vision of creating wealth from our renewable biomass resources with the drive to make our world more sustainable.

Acknowledgments

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