Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential

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National Renewable Energy Laboratory

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Technical Report
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Acronyms

3-HPA	3- 3-Hydroxypropionic acid
APR	aqueous phase reforming
BC	biochemical
BD	1,3-butadiene
BDO	1,4-butanediol
BETO	Bioenergy Technologies Office
BTX	mixed xylenes/aromatics
DMF	dimethylfuran
DMT	dimethyl terephthalate
DOE	U.S. Department of Energy
ECH	epichlorohydrin
EIA	Energy Information Administration
EPA	U.S. Environmental Protection Agency
FA	furfuryl alcohol
FAF	furfural-acetone-furfural
FCC	Food Chemicals Codex
FDA	U.S. Food and Drug Administration
FDCA	furan-2,5-dicarboxylic acid
GBL	gamma-butyrolactone
GDP	gross domestic product
GRAS	Generally Recognized as Safe
HDPE	high-density polyethylene
IPO	initial public offering
LCI	life-cycle inventory
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MF	2-methylfuran
MM	million
MTBE	methyl tertiary butyl ether
MTHF	2-methyltetrahydrofuran
PBT	polybutylene terephthalate
PDO	1,3-propanediol
PEF	polyethylene furanoate
PET	polyethylene terephthalate
PG	propylene glycol
PGI	propylene glycol industrial grade
PHA	polyhydroxyalkanoate
PI	polyisoprene
PLA	polylactic acid
PO	propylene oxide
PTA	purified terephthalic acid
PTT	polytrimethylene terephthalate
PVC	polyvinyl chloride
pX	para-xylene or xylene (para)
R&D	research and development
REACH	Registration, Evaluation and Authorization of Chemicals
SBR	styrene-butadiene rubber
SIS	styrene-isoprene-styrene
SNAP	Significant New Alternatives Policy
TA	terephthalic acid
TC	thermochemical
TC/BC	hybrid thermochemical/ biochemical
TEA	techno-economic analysis
THF	tetrahydrofuran
THFA	tetrahydrofurfuryl alcohol
TRL	technology readiness level
USDA	U.S. Department of Agriculture
USP	U.S. Pharmacopeia

Executive Summary

As outlined by the U.S. Department of Energy Bioenergy Technologies Office, biomass "utilization for fuels, products, and power is recognized as a critical component in the nation's strategic plan to address our continued dependence on volatile supplies and prices of imported oil" (Bioenergy Technologies Office 2015).

Production of chemicals from biomass offers a promising opportunity to reduce U.S. dependence on imported oil, as well as to improve the overall economics and sustainability of an integrated biorefinery. In considering petroleum refinery economics, 15% of the entire barrel of oil goes toward the production of chemical products, while chemical products account for nearly 50% of the profits (Bioenergy Technologies Office 2014, Rinaldi and Schuth 2009). Chemical production, however, also has a big impact on the overall sustainability of a refinery process. As reviewed in recent International Energy Agency reports, the chemicals industry accounts for 30% of the total industrial energy demand worldwide and is responsible for 20% of the industrial greenhouse gas emissions (IEA 2013). There are therefore clear opportunities to positively impact the economics and sustainability of an integrated biorefinery by displacing/replacing fossil-derived chemicals with bio-derived products and, in response, the market for bioproducts is expected to grow over the next several decades. Recent analysis projects the market share of bio-based chemicals in the global chemical industry will increase from 2% in 2008 to 22% in 2025, and the market potential for bio-based chemicals will be $19.7 billion in 2016 (Bergeson, Auer, and Peveler 2012, Lux Research 2011, Williamson 2010).

This report assesses the increased momentum towards the deployment and scaled-up production of bio-derived chemicals by:

- **Reviewing the broad range of chemicals that can be produced from biomass.** The report summarizes the current state of the field, and presents a list of products that can currently be made from biomass via a spectrum of conversion routes including biochemical, thermochemical and algal. The list of chemicals considered is not intended to be comprehensive, but rather focused on products with clear near-term market potential.
- **Focusing on a subset of 12 chemicals with prospects for near-term deployment.** This study highlights the approaches and criteria used to identify which products have the potential for near-term deployment based on their current state of development, as well as market considerations.
- **Providing a detailed discussion of the existing markets and future potential for each of the bioproducts.** For the selected bioproducts, the report strives to:
    1. Understand the competition with fossil-derived products by identifying existing and projected markets, key producers and consumers, and the primary downstream applications and end-usage.
    2. Identify the production leaders who are actively scaling up chemical production routes from biomass.
    3. Review the consumers and market champions who are supporting these efforts.

4. Understand the key drivers and challenges to move biomass-derived chemicals to market.
5. Summarize the opportunities for these biomass-derived chemicals as both direct and functional replacements.
6. Evaluate the impact that scale-up of chemical manufacturing strategies will have on accelerating the production of biofuels.

The biomass-derived products that are reviewed in detail in this report include 1,4-butanediol, 1,3-butadiene, ethyl lactate, fatty alcohols, furfural, glycerin, isoprene, lactic acid, 1,3-propanediol, propylene glycol, succinic acid, and para-xylene. Emerging products including adipic acid, acrylic acid, and furan-2,5-dicarboxylic acid are also discussed. The report draws upon publically available information at the time of development.

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Introduction

Production of chemicals from biomass offers a promising opportunity to improve the overall economics and sustainability of an integrated biorefinery while reducing U.S. dependence on imported oil. As recently reported in a study sponsored by the U.S. Department of Agriculture (USDA), in 2013 the overall bio-based products industry supported four million jobs with a value of $369 billion to the U.S. economy (Golden et al. 2015). Another USDA-sponsored report found that bio-based products currently displace about 300 million gallons of petroleum per year, which is equivalent to taking 200,000 cars off the road (Golden and Handfield 2014). Based on current growth, the market for bio-based chemicals is projected to reach $19.7 billion in 2016 (Bergeson, Auer, and Peveler 2012, Lux Research 2011, Williamson 2010). Argonne National Laboratory completed a series of analyses to understand the sustainability impacts of a range of bioproducts and demonstrated a reduction in greenhouse gas emissions for bio-derived products relative to their petroleum counterparts (Dunn et al. 2015).

Here, this report presents the results of a market assessment aimed at identifying promising bioproducts that can be deployed in the near-term. Bioproducts are value-added chemicals or materials derived from renewable sources such as commodity sugars, lignocellulosic biomass, or algae. The focus of this assessment is on bio-derived chemicals that are either finished products that are ready for use (e.g., solvents) or intermediates that become a feedstock for further processing. Bioproducts may compete with petroleum-based chemicals as drop-in replacements or they may provide unique, functional replacements that can only be produced from biomass. Based on recent economic evaluations of the technology pathways focused on the production of hydrocarbon biofuels, drop-in and functional replacement bioproducts will be important drivers for developing an economically viable and sustainable biorefinery (Davis et al. 2013). The diversity of bioproducts, with their wide range of markets and applications, requires individual case studies of each product as described below.

Table 1. Biomass-Derived Chemicals Selected for Initial Evaluation

Acetic Acid	Epichlorohydrin	Glycerol	Phenol
Acetone	Ethyl Acetate	3-HPA	Propanediol
Acrylic Acid	Ethyl Lactate	Isoprene	Propylene Glycol
Acrylonitrile	Ethylene	Lactic Acid	Sorbitol
Adipic Acid	Fatty Acids	Levulinic Acid	Succinic Acid
Benzene	Fatty Alcohols	Lipids	THF
Butanediol (1,4-)	FDCA	Oxo Chemicals	Xylene (para)
Butadiene (1,3-)	Furfural	PHA	Xylitol

The market analysis performed here began with a literature review of current pathways for biomass-derived chemicals being pursued at research and development (R&D) and deployment/commercialization stages. Based on this review, 32 biomass-derived chemicals were identified (Table 1). The goal was to identify the current market volumes, prices, and projected growth for each of these products in the United States and globally, as well as to evaluate the potential for a near- to midterm deployment of these bio-derived chemicals.

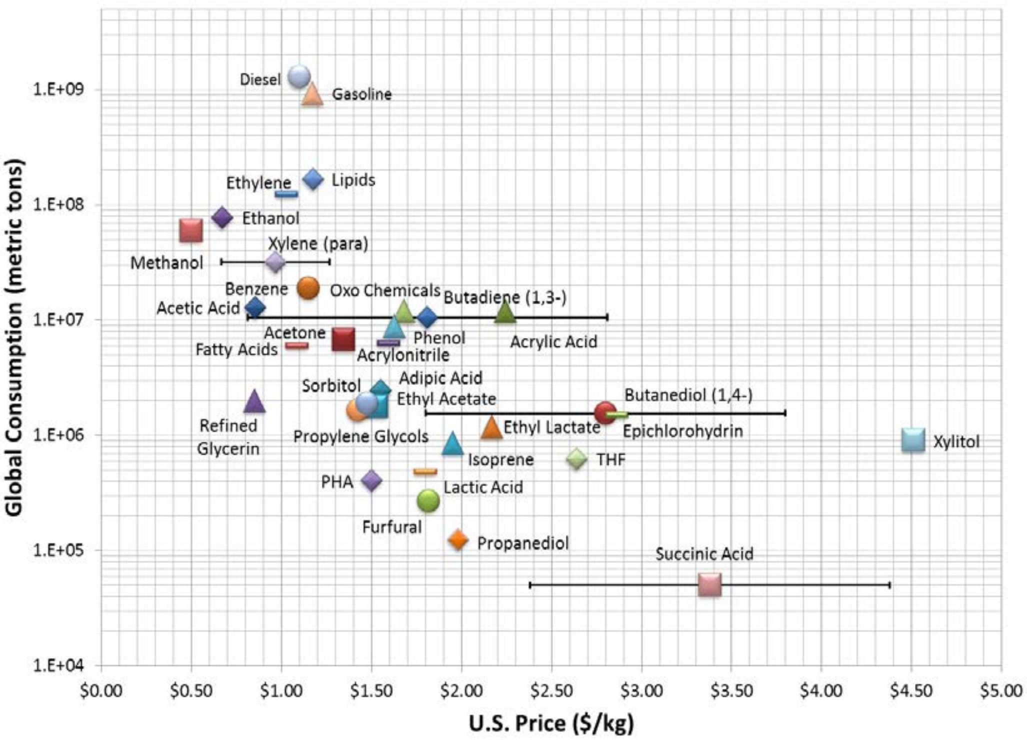

Figure 1. A summary of reported U.S. market price versus annual global volume for selected chemicals. The 3-5 year average price is provided. Error bars are shown for chemicals with large fluctuations in prices. Most chemical prices had a standard deviation of $0.30/kg or less. For reference, 1.3 billion metric tons of diesel is equivalent to 390 billion gallons. The price for ethanol was assumed to be $2/gallon.

The results of the preliminary analysis indicate that there is a broad range of global consumption, prices, and markets for the identified chemicals (Figure 1, (Terry 2015, Dietrich 2015a, 2015a, 2012d, Packham 2014, Ng 2015, Wang 2015a, Clark 2015a, Kelley 2013, 2012b, Terry 2013a, 2012, 2014a, Dietrich 2013b, 2012, Terry 2014b, Hall 2015a, Bewley 2011, 2012c, Lemos and Yost 2013, Dietrich 2013a, Dang 2014, Toledo 2015, Yanelli 2015, Clark 2015b, 2011, Terry 2014c, 2013b, Hall 2015b, Lim 2015, IHS 2015a, Mordor Intelligence LLP 2015a, Future Market Insights 2015, American Chemical Society 2015, Mordor Intelligence LLP 2015b, McCloskey 2014, Rakes 2014, Carmody 2015, Taylor 2010, Grand View Research 2015, GlycosBio 2010, ICIS 2008, Quispe, Coronado, and Carvalho 2013, Wang 2013, 2012, Dang 2015, 2012b, Balboa 2012, Martin 2014, Waldheim 2015, Pafford 2014, 2015, de Guzman 2010a, 2015b, 2014d, Wang 2015b, Dietrich 2014d, Kelley 2012a, Dietrich 2014a, c, Mirasol 2015, Dietrich 2015b, Solutions 2015, Kirschner 2007, Gan 2013)). Chemical products are priced on a mass basis ($/kg) and the reported values are contract prices that have been averaged over 3-5 years. For comparison, a five year average of regular gasoline at $3.29/gallon and diesel at \$3.65/gallon is equivalent to \$1.17/kg and \$1.10/kg, respectively[1]. A promising point to note is that a number of bioproducts have values much greater than gasoline or diesel fuel products. A challenge with these single-point assessments, however, is that these are inherently commodity markets, with prices and consumer demands that fluctuate; therefore this report summarizes major drivers for these complex and unpredictable markets.

Fuels and Chemicals Value Chain

Chemical markets are diverse and complex relative to fuel markets. Traditional chemical manufacturers operate along a value chain (i.e., supply chain) from a lower value/higher volume feedstock like petroleum, natural gas, or basic petrochemicals to lower volume/higher value categories like polymers, specialty chemicals, and active ingredients. Connections between chemicals along the value chain are linked as a product tree based on their chemical precursors (Kannegiesser 2008). The product tree concept is common in the chemicals industry where a single chemical precursor (often referred to as a platform chemical) can be further converted to higher value or larger market derivatives. Figure 2 illustrates the value chain concept for ethylene, a key platform chemical in the petrochemical industries. As also highlighted in Figure 2, chemical products are typically used across multiple industries (e.g., for coatings, polymers, pharmaceuticals, packaging, and coolants).

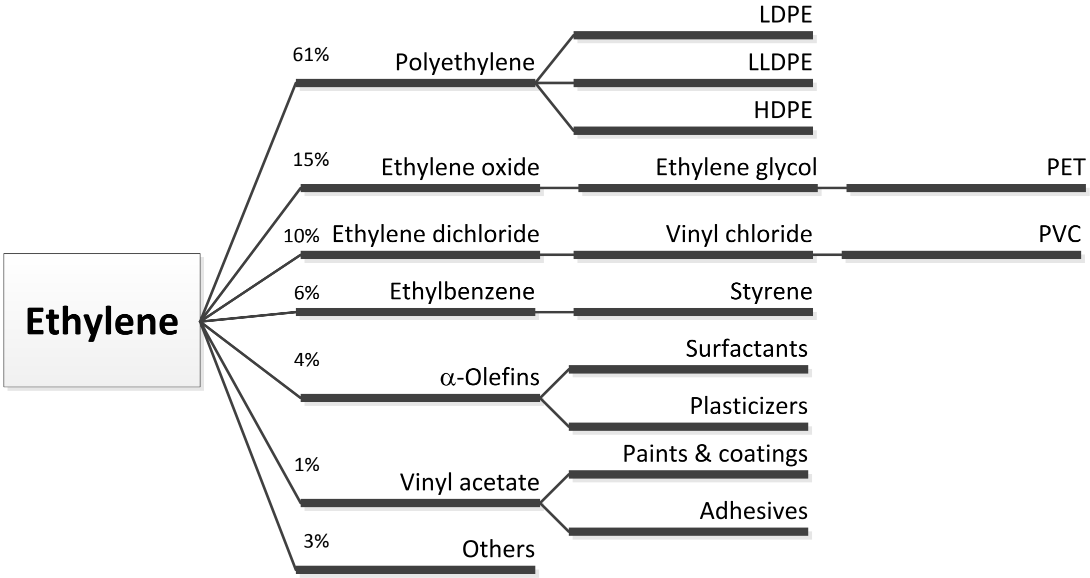

Figure 2. Ethylene and its downstream products are an example of a product tree in the chemical industry (Matar and Hatch 2001). The relative percent flow of ethylene (more than 100 million metric tons/year) to downstream products is shown on the tree. (Abbreviations: LDPE is low-density polyethylene, LLDPE is linear low-density polyethylene, HDPE is high-density polyethylene, PET is polyethylene terephthalate, and PVC is polyvinyl chloride.)

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[1] Energy Information Administration (EIA) price data are a 5-year average for all grades of gasoline and diesel fuel (www.eia.gov/dnav/pet/pet_pri_gnd_dcus_nus_w.htm);
Reformulated gasoline density was assumed to be 2.819 kg/gal and diesel was 3.167 kg/gal (http://cta.ornl.gov/bedb/appendix_a/Lower_and_Higher_Heating_Values_of_Gas_Liquid_and_Solid_Fuels.pdf).

An analogous value chain for biomass-derived chemicals would start with lower value/higher volume categories like cellulosic feedstocks, sugars, or syngas and extend to lower volume/higher value categories like commodity chemicals, green solvents, or renewable polymers. Product trees have been proposed in previous studies for bioproducts where carbohydrates, lignin, lipids, and protein from biomass could be converted to a variety of chemicals, again where each one can either serve as an intermediate or as a final product (Figure 3). Similar to petrochemicals, some of the chemicals under the "Building Blocks" heading in Figure 3 have also been referred to as platform chemicals (e.g., succinic acid) (Bozell and Petersen 2010).

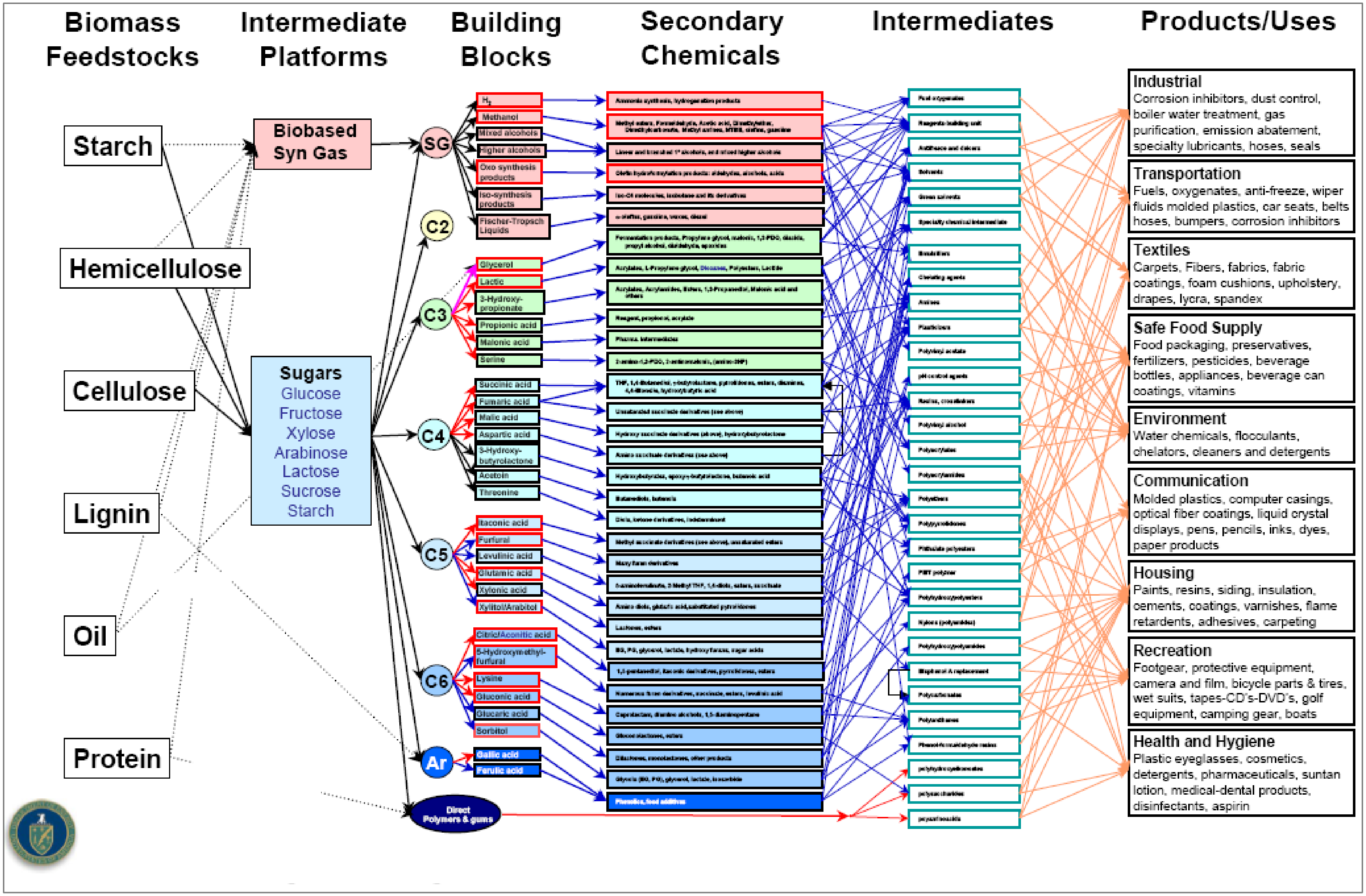

Figure 3. A product tree for bioproducts where carbohydrates, lignin, oil, and protein from biomass can be converted to a variety of chemicals and products (Werpy, Holladay, and White 2004)

Selection of the Products for Further Assessment

Twelve of the previously highlighted 31 products were selected for further review and are discussed in more detail in this report. The selected products were considered to have higher potential for near-term deployment. Not all of these products fit neatly into a single product tree, but rather range from platform chemicals to downstream products.

Initially a number of key metrics were identified that could lead to the successful near-term deployment of biomass-derived chemicals (Table 2). The targeted products were considered in the context of:

- Sufficiently high market volume and value (greater than fuel). Both domestic and global current market share and growth potential were evaluated for each bioproduct.
- A well-established and mature market, since this could have a significant impact on the near-term deployment. Platform chemicals were considered advantageous as there was a potential for a greater market development.
- Feedstock flexibility.
- Potential to be integrated with representative hydrocarbon conversion pathways supported by the U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) program.
- Ongoing or prior support for research and development of each of these products from the DOE, which was considered favorable since many of these projects focused on lignocellulosic feedstocks.
- Avoidance of products that would be in competition with natural gas-derived petrochemicals. Inexpensive natural gas in the United States has changed the chemicals market, as it has greatly reduced the cost and increased the production for a number of petrochemicals. Any bioproduct that directly competes with natural gas-derived chemicals would be disadvantaged.
- Chemicals that could be made at a lower cost from biomass versus petroleum were deemed to have a favorable bioprocess advantage.

Table 2. Criteria by which the Market Potential of Bioproducts Was Evaluated

High volume/value	Market maturity	High growth (domestic)
High growth (global)	Feedstock flexibility	Platform chemical
DOE interest/funding	Integrated with representative hydrocarbon conversion pathways	Avoids competition with natural gas
Market pull	End user specifications	Bioprocess advantage
Current scale	Favorable life cycle	Near-term deployment (high TRL level)

COMPETITION WITH NATURAL GAS AND SHALE GAS

As highlighted in the downselect discussion, one of the decision-making criteria applied when reviewing the possible bioproduct pathways is competition with natural gas. With EIA projecting low-cost natural gas for the foreseeable future, bioproducts will be at an economic disadvantage relative to chemicals produced from natural gas simply due to the differences in feedstock costs (U.S. Energy Information Administration 2015). One such example is methanol and methanol derivatives (Spath and Dayton 2003). With low cost natural gas, projections suggest that the United States may see an additional 33 million metric tons of methanol capacity in the next decade, which is more than eight times the current domestic output (Tullo 2014b). Therefore, the market competition for biomass-derived methanol and derivatives, such as acetic acid, will be challenging.

Low-cost shale gas, however, may provide opportunities for biomass-derived chemicals, especially for C4 and C5 chemicals such as isoprene and butadiene (Coons 2014c). These chemicals are traditionally byproducts of ethylene production and are produced in higher yields when heavier feedstocks such as naphtha are converted (Donald L. Burdick 2001). Ethylene is currently being produced via cracking of these lighter shale gases, which results in high yields of ethylene but low yields of these commercially important byproducts. Consequently, there has been a constrained supply of chemicals, including butadiene and isoprene, over the past several years, which has led to large price fluctuations and increased the market potential for bio-derived products.

Many of the identified criteria have been used in previous studies, including the top 10 value-added chemicals analysis (Bozell and Petersen 2010, Werpy, Holladay, and White 2004, Holladay, Bozell, et al. 2007); however, the set of key criteria was expanded to identify areas in which there is potential to accelerate these chemicals to market more rapidly. For example, the existence of potential market champions that can drive and financially support the growth of these biomass-derived chemicals and influence market expansion was considered. This analysis also began examining sustainability drivers by reviewing existing life-cycle inventories (LCIs) for petroleum-derived products. Further, chemicals that could integrate with the representative hydrocarbon pathways currently being considered in the DOE BETO-supported research and development efforts were preferentially considered. Moreover, products that are being scaled-up were assigned a lower risk and greater near-term potential than bench-scale or conceptual bioproducts.

Defining “Near-Term”

The primary focus of this report, and major factor in the selection of products for further review, is on products that have near-term deployment potential. This focus aligns well with goals to deploy biofuels at scale in the near term, and utilizes coproducts to enhance both process economics and sustainability in a biorefinery (Davis et al. 2013).

Technology readiness level (TRL in Table 3) of a given process can be used to evaluate if it has the potential to be deployed in the near term. A TRL of 6 or greater was used as a proxy for near-term deployability in this report. Processes at TRL 6 have reached pilot scale. Pilot-scale demonstrations require prototype process equipment and testing is typically done on relevant feedstocks in an integrated manner. This is a major step in a technology's demonstrated readiness. At TRL 6, testing has advanced from laboratory scale to engineering scale where the testing process parameters closely match expected larger scale parameters (DOE 2011). Successful pilot-scale testing can lead to larger scale demonstration and deployment.

Table 3. Department of Energy Technology Readiness Levels (DOE 2011)

TRL Level	Scale of Testing	Fidelity	Environment [A],
9	Full	Identical	Operational (Full Range)
8	Full	Identical	Operational (Limited Range)
7	Full	Similar	Relevant
6	Engineering/Pilot Scale	Similar	Relevant
5	Lab/Bench	Similar	Relevant
4	Lab	Pieces	Simulated
3	Lab	Pieces	Simulated
2		Paper	
1		Paper	

(A) Simulants should match relevant physical and chemical properties.

The bioproducts selected for further analysis are listed in Table 4. The TRL levels are based on public reports using commodity feedstocks like starch, sugar, and plant-based lipids. The bioproducts are classified by type where drop-in chemicals are identical to those currently on the market. Functional replacements differ from products that are currently available, but have superior properties with similar applications that help drive market demand. One of the challenges for market penetration of functional replacements is that they require significant property testing to allow displacement of the molecule currently being used.

The bioproducts that were not chosen for further consideration were eliminated for a variety of reasons, including a low TRL level (acrylonitrile), lack of current efforts being funded on biomass-focused research (benzene, phenol), directly competing with natural gas (acetic acid, ethylene , ethyl acetate), an existing market that is saturated utilizing commodity feedstocks (sorbitol, xylitol), issues with market attractiveness (acetone, levulinic acid, polyhydroxyalkanoates [PHAs]), or could be produced from one of the selected products (such as tetrahydrofuran [THF] from 1,4-butanediol or epichlorohydrin from glycerol). A number of products, including acrylic acid, furan-2,5-dicarboxylic acid (FDCA), and acetic acid, that have been developed and are undergoing pilot-scale demonstration and show potential for further development and scale-up, are also highlighted within the report.

Bioproducts can be produced through a wide range of conversion platforms including biochemical (BC), thermochemical (TC), hybrid thermochemical/biochemical (TC/BC) and algal routes. Table 4 summarizes the potential conversion pathways for each bioproduct considered in the final selection process.

Table 4. Summary of Chemicals Suggested for Market Analysis. The chemical type describes whether a bioproduct is a drop-in (identical molecule) or functional (has similar properties) replacement for the traditional fossil source. The TRL levels are based on public reports using commodity feedstocks like starch, sugar, and plant-based lipids. The alignment between each bioproduct and biomass conversion platform is also included. Finally, it is indicated if R&D efforts are on-going for lignocellulosic feedstocks (since R&D efforts may not be publically disclosed, a definitive No was not included in this category).

Chemical	Type	Conversion Pathway	TRL Level (based on commodity feedstocks)	R&D (ongoing for lignocellulosic feedstocks)
Butadiene (1,3-)	Drop-in	BC–Biological TC/BC–Gasification/Fermentation	6	Y
Butanediol (1,4-)	Drop-in	BC–Biological	8	Y
Ethyl Lactate	Functional	BC–Biological	9	Y
Fatty Alcohols	Drop-in	TC–Gasification, BC–Biological, Algae	9	
Furfural	Functional	TC–Pyrolysis, BC–Catalytic	9	Y
Glycerol	Functional	Algae	9	
Isoprene	Drop-in	BC–Biological	6	
Lactic Acid	Functional	BC–Biological	9	Y
Propanediol (1,3-)	Functional	BC–Biological	9	
Propylene Glycol	Functional	BC–Biological	9	
Succinic Acid	Functional	BC–Biological	9	Y
Xylene (para)	Drop-in	BC–Catalytic TC–Pyrolysis	6	Y

In a number of cases, companies are working toward the development of processes for lignocellulosic biomass conversion. The goal of many of these efforts is to enable a diversification of feedstocks to allow for future cost savings. As highlighted in various sections of the report, there are inherent challenges that companies face when utilizing lignocellulosic feedstocks due, in part, to impurities that can be introduced in the process and the impact that such impurities have on process separation/purification steps and the ability to meet product purity specifications that are more stringent than traditional fuel specifications. A list of examples is provided here:

- Genomatica has investigated the production of bio-based 1,4-butanediol utilizing lignocellulosic sugars from a variety of pretreatment technologies (Genomatica 2015b).
- INVISTA is working with LanzaTech to utilize syngas fermentation to 2,3-butanediol with further catalytic conversion to butadiene.
- Furfural is produced commercially from bagasse and cobs by a number of companies (International Furan Chemicals 2014b).
- Archer Daniels Midland (ADM) and others have commercial-scale production of glycerol from natural lipids (ADM 2014b).
- Amyris expects to begin commercializing bio-isoprene from sugarcane (Amyris 2014).
- Lactic acid is commercially available from NatureWorks and Purac (NatureWorks 2014a).
- Cellulac has produced commercial quantities of lactic acid from agricultural residues (Cellulac 2015). They could feasibly produce ethyl lactate from agricultural residues as well.
- BioAmber has developed licensing agreements with Cargill to adopt a yeast microorganism that is reportedly able to utilize a range of lignocellulosic feedstocks (Nexant 2012, Jansen and van Gulik 2014).
- Renewable para-xylene is being pursued via a thermochemical catalytic fast pyrolysis route by Anellotech, which can utilize a range of cellulosic convertible feedstocks.

Finally, this report was developed utilizing the best available public information at the time of publication. Additional products, the details of which remain proprietary, may be under development by chemical firms and bioproduct producers.

Brief Overview of Selected Bioproducts

The selected bioproducts are briefly introduced below. Because a primary focus of this analysis is the impact that biomass-derived chemicals can have on the U.S. economy, the locations of current and planned facilities for these specific products are summarized in the Figure 4 map. More detailed information on each of these products is presented in subsequent sections of this report.

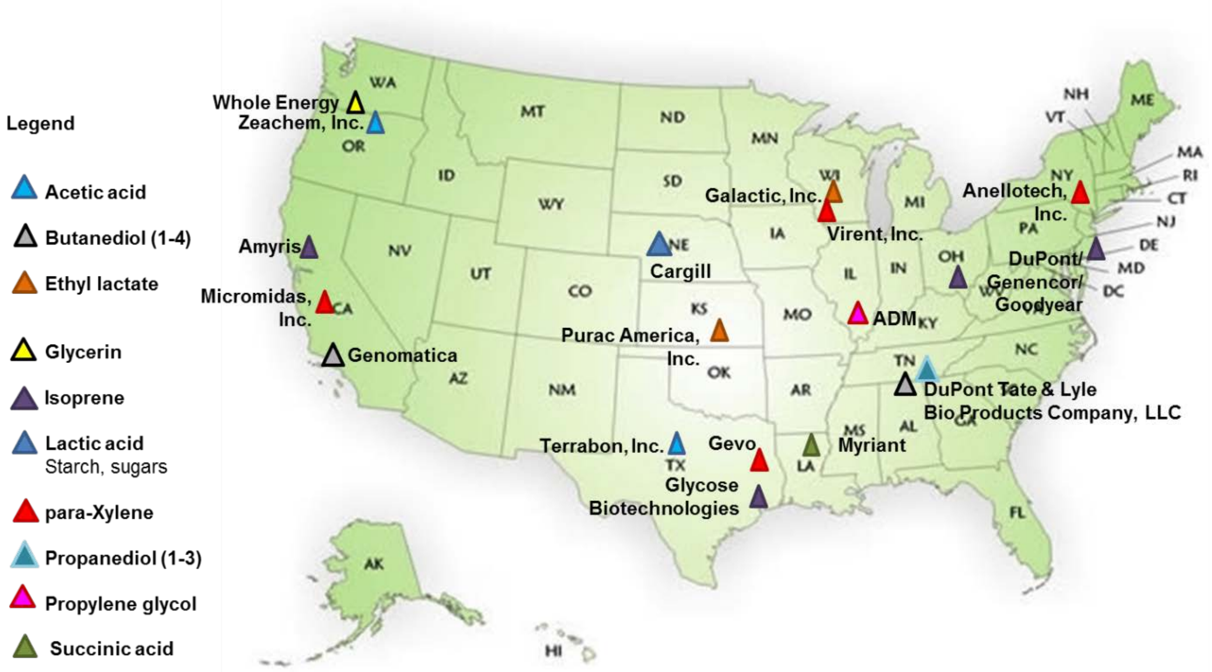

Figure 4. Overview of current and planned bioproduct facilities in the United States

Butadiene (1,3-)

1,3-butadiene (BD) is the building block for the production of polybutadiene and styrene-butadiene rubbers, which are used in the production of tires for passenger cars and light-duty vehicles. Butadiene is currently produced from petroleum as a byproduct of ethylene manufacturing. However, the shift to lighter feedstocks in ethylene production due to the abundance of shale gas has resulted in a constrained supply of butadiene and large price fluctuations over the past several years, thus providing an opportunity for bio-derived butadiene. There are multiple biomass conversion strategies for the production of a direct renewable butadiene replacement. These efforts are primarily being pursued by smaller start-up companies through investments by large international chemical producers, including companies like Braskem, INVISTA, Synthos, and Versalis.

Butanediol (1,4-)

1,4-butanediol (BDO) is a four-carbon primary alcohol that is a building block for the production of polymers, solvents, and specialty chemicals. Current demand for BDO is just under 2 million metric tons per year. With this large market, and with market champions including Nike and INVISTA utilizing renewable sources for the production of polymers, bio-derived BDO is being produced on a commercial scale utilizing commodity sugars by BASF. Genomatica has led efforts to develop technology to directly produce BDO and, with support from the DOE, the company has successfully demonstrated an integrated process utilizing a range of lignocellulosic sugars that has commercialization potential. Another promising conversion strategy currently being scaled-up is the catalytic conversion of succinic acid to BDO.

Ethyl Lactate

Ethyl lactate is a biodegradable solvent produced by the esterification of ethanol and lactic acid. It was listed as part of the U.S. Environmental Protection Agency's (EPA's) Significant New Alternatives Policy (SNAP) as a solvent that meets the ozone protection provisions of the Clean Air Act (EPA 2015b, EIA 2014). It has been used in industrial applications to replace volatile organic petroleum-derived compounds. The primary use for ethyl lactate is as an industrial solvent, as its properties and performance have been found to meet or exceed those of traditional solvents like toluene, methyl ethyl ketone, and N-methyl-pyrrolidone in many applications. The estimated demand for all solvents in the United States is approximately 5 million metric tons annually. Ethyl lactate is expected to compete effectively in that market as economies of scale and process or supply chain improvements drive down costs. It has been the subject of hundreds of journal articles and has attracted attention because both of the starting materials used to make ethyl lactate, lactic acid and ethanol, have a high potential to be made from lignocellulosic sugars.

Fatty Alcohols

Fatty alcohols, also called detergent alcohols, are linear alcohols of 12 or more carbons, used primarily to produce anionic and non-ionic surfactants for household cleaners, personal care products, and industrial applications. Shorter chain alcohols, in contrast, are used most often as plasticizers. Fatty alcohols accounted for 11% of current bio-based chemicals in commercial production. Fatty alcohols are derivatized by ethoxylation, sulfation, or sulfonation before use. They can be produced from tallow, vegetable oils, or petroleum. Each of these classes of feedstocks can be substituted for one another (i.e., as functional replacements) and the market for detergent alcohols is price sensitive. This has led to rapidly changing geographic shifts in detergent alcohol production and an overall move to price-competitive plant-derived feedstocks. Fatty alcohols have the potential to be produced from renewable sources by autotrophic and heterotrophic algae, or by the microbial fermentation of carbohydrates.

Furfural

Furfural is a heterocyclic aldehyde, produced by the dehydration of xylose, a monosaccharide often found in large quantities in the hemicellulose fraction of lignocellulosic biomass. In theory, any material containing a large amount of pentose (five-carbon) sugars, such as arabinose and xylose, can serve as a raw material for furfural production. Most furfural is converted to furfuryl alcohol (FA), which is used for the production of foundry resins. The anti-corrosion properties of FA make it useful in the manufacture of furan fiber-reinforced plastics for piping. Furfural has a broad spectrum of industrial applications, such as the production of plastics, pharmaceuticals, agro-chemical products, and non-petroleum-derived chemicals. Furfural is not produced from fossil feedstocks, therefore current production methods from biomass do not displace production from petroleum. However, recent research has reported a furfural-to-distillate fuel pathway that could potentially make furfural derivatives a drop-in replacement for petroleum-derived distillate fuels (jet and diesel). Furfural demand in the United States is not expected to grow significantly, therefore the primary market driver for the production of furfural may be conversion to jet and diesel fuel blendstocks.

Glycerin

Glycerin is a polyhydric alcohol and is a main component of triglycerides found in animal fats and vegetable oil. The word ‘glycerin’ generally applies to commercial products containing mostly glycerol, whereas the word “glycerol” most often refers specifically to the chemical compound 1,2,3-propanetriol and to the anhydrous content in a glycerin product or in a formulation. Glycerin is the main byproduct of biodiesel production. It is also generated in the oleochemical industry during soap production and is produced synthetically from propene. Biodiesel and soap production accounts for most current glycerin production; therefore, the overall supply of glycerin is driven primarily by the demand for these products. Glycerin from biomass is a drop-in replacement for synthetic glycerin from propene. The most common use is as a humectant (hygroscopic substance) in food and personal care products, but it has more than 1,500 uses. The glycerin market is currently saturated, which has resulted in stable and low glycerin prices. As a result, the primary market driver for producing glycerin may be leveraging the low, stable prices by using it as a feedstock for conversion to more valuable products, such as epichlorohydrin and succinic acid. The low, stable prices may also allow emerging uses, such as for animal feed and marine fuel.

Isoprene

Isoprene is the building block for polyisoprene rubber, styrene co-polymers, and butyl rubber. Currently all commercially available isoprene is derived from petroleum. The majority of isoprene has typically been produced by separating the C5 stream from ethylene crackers fed with heavier feedstocks like naphtha or gas oil. Recently, steam crackers in the United States have shifted toward using lighter feedstocks like ethane, propane, and butane, which are byproducts of shale gas production. These lighter feedstocks have increased ethylene yields but have negatively impacted isoprene production. This has created a favorable opportunity for bio-based isoprene to enter the market. Bio-based isoprene, produced by aerobic bioconversion of carbohydrates, is identical to petroleum-based isoprene and functions as a drop-in replacement molecule. Production of isoprene from biological sources is in the early stages of development but is accelerating with the backing from major tire manufacturers (Bridgestone, Goodyear, and Michelin).

Lactic Acid

Lactic acid is the most frequently occurring carboxylic acid in nature. Most commercial production of lactic acid is by microbial fermentation of carbohydrates. It is an alpha-hydroxy acid with dual functional groups making it suitable for use in a variety of chemical transformations and products. Lactic acid is used globally for applications in food, pharmaceuticals, personal care products, industrial uses, and polymers. Growth in polylactic acid polymer production is expected to drive growth for lactic acid consumption. The biodegradable polylactic acid has gained popularity for use in food packaging, disposable tableware, shrink wrap, 3-D printers, and elsewhere.

Propanediol (1,3-)

1,3-propanediol (PDO) is a linear aliphatic diol, which makes it a useful chemical building block. It has attracted investment for production from both petroleum and renewable feedstocks. PDO can be used for a variety of applications including polymers, personal care products, solvents, and lubricants (Vilela et al. 2014, Zeng and Sabra 2011). A major driver for PDO production is as a component in polytrimethylene terephthalate (PTT) polymers. PTT is used in textiles and fibers due to its superior durability and stain resistance compared to nylon (Corma, Iborra, and Velty 2007). PDO has been produced synthetically from acrolein or ethylene oxide, but today bio-based PDO is the primary source of production. DuPont Tate & Lyle Bio Products Company is the largest producer of bio-based PDO. Bio-based PDO uses 40% less energy than the typical petroleum-based route, giving the bio-based route a significant advantage.

Propylene Glycol

Propylene glycol (PG) is a diol (i.e., two hydroxyl groups) also known as 1,2-propanediol, propane-1,2-diol, and monopropylene glycol. It is a viscous, colorless, odorless liquid that does not evaporate (nonvolatile) at room temperature and is completely soluble in water (DOW 2013). PG is safe for human consumption, and therefore is used in the production of consumer products such as antiperspirants, suntan lotions, eye drops, food flavorings, and bulking agent in oral and topical drugs (ADM 2015c). Industrial grade propylene glycol (PGI) is used in the production of unsaturated polyester resins for end use markets such as residential and commercial construction, marine vessels, passenger vehicles, and consumer appliances (IHS 2014b). PG is also used as an engine coolant and antifreeze in place of ethylene glycol, and in the airline industry as an airplane and runway de-icer. In liquid detergents, PG serves as a solvent, enzyme stabilizer, clarifying agent, and diluent (ADM 2015e). Conventional PG has been produced by hydrating propylene oxide (PO), although bio-PG can be produced by hydrogenolysis of glycerin over mixed-metal catalysts, or hydrocracking of sorbitol. Bio-PG is a drop-in replacement for conventional PG. A primary driver of bio-PG production is profitable disposition of excess glycerin coproduct of biodiesel production. Companies pursuing bio-PG in the United States include ADM, Ashland, and Cargill (Grand View Research 2013).

Succinic Acid

Succinic acid is a dicarboxylic acid that can be produced from petroleum or biomass. The current market for petroleum-derived succinic acid is small with a primary focus on specialty chemicals. The potential for biomass-derived succinic acid is projected to be large, however, as a possible precursor for the synthesis of high-value products derived from renewable resources, including commodity chemicals, polymers, surfactants, and solvents. Due to the large market potential for succinic acid, production facilities have started operation in the past three years utilizing biomass feedstocks with a combined capacity of 55,000 metric tons/year, which is very close the current market for petroleum-derived succinic acid. If all announced projects are completed within the next three years, a total of 140,000 metric tons/year of renewable succinic acid will be available worldwide. A number of additional facilities are planned and the future worldwide production capacity of succinic acid is projected to be more than 400,000 metric tons/year.

Xylene (para)

Para-xylene (pX) is used to produce both terephthalic acid (TA) and dimethyl terephthalate (DMT). Both TA and DMT are raw materials for the production of polyethylene terephthalate (PET) bottles. Major consumers of PET bottles, including Coca-Cola and PepsiCo., are supporting efforts to develop renewable bottles on a targeted timeline and by actively funding R&D efforts for the production of renewable PET. The renewable replacements that are currently being developed include a direct replacement of petroleum-derived pX from biomass or via functional replacements of PET (such as polyethylene furanoate). Renewable pX can be produced via the traditional biochemical fermentation process followed by upgrading, thermochemical pyrolysis routes, and hybrid thermochemical/biochemical strategies of catalytic upgrading of sugars.

Butadiene (1,3-)

1,3-butadiene (Figure 5) is a four-carbon (C4) building block for the production of rubber that is primarily used in the production of tires for passenger cars and light-duty vehicles. Butadiene is currently produced from petroleum as a byproduct of ethylene manufacturing. However, the shift to lighter feedstocks in ethylene production, due the abundance of shale gas and a concomitant reduction in naphtha cracking, has resulted in a constrained supply of butadiene and large price fluctuations over the past several years opening the potential for bio-derived butadiene. There are multiple biomass conversion strategies for the production of a direct renewable butadiene replacement. These efforts are primarily being pursued by smaller start-up companies through investments by large international chemical producers including Braskem, INVISTA, Synthos, and Versalis.

Figure 5. The chemical structure of 1,3-butadiene (C_4H_6)

Production from Petroleum

There are multiple routes for the production of 1,3-butadiene (Figure 6). The primary route utilized in the United States is as a byproduct recovered in the production of ethylene and propylene. The cracking of heavy feedstocks such as naphtha or gas oil produces roughly 1 pound of butadiene for every 7 pounds of ethylene, where the conversion of lighter feedstocks like ethane produces 1 pound of butadiene for every 45 pounds of ethylene produced (Burdick 2010). The shift to lighter feedstocks in cracking processes due to the low cost and abundance of shale gas has resulted in lower yields of butadiene and made recovery uneconomical (Coons 2014b). Ethylene producers who do not directly extract the butadiene will sell a crude C4 stream with a mix of products. Companies like Shell, ExxonMobil, and TPC Group are key processors of these purchased crude C4 streams for butadiene recovery.

With the increasing demand and higher prices for butadiene due to this shift to lighter cracking feedstocks, other technologies have shown the potential to be economically viable. Butadiene can be produced via dehydrogenation of n-butane or n-butene. The TPC Group is currently working to build a commercial facility for the production of butadiene from butenes that is expected to come online in 2016 (Yost 2013). UOP and TPC Group have announced a joint partnership, as have Linde and BASF, for developing licensing opportunities for the production of butadiene via these routes (UOP 2014b, BASF 2014).

The top producer and consumer of butadiene is China with all of Asia (China, Japan, the Republic of Korea, India, Indonesia, Malaysia, Singapore, Taiwan, and Thailand) producing roughly 50% of the world’s supply. Europe (Austria, Belgium, Finland, France, Germany, Italy, the Netherlands, Portugal, Spain, and the United Kingdom) ranks second in production and consumption while the United States ranks third. The top producers in the United States include TPC Group, LyondellBasell, Shell, and ExxonMobil (Yost 2013).

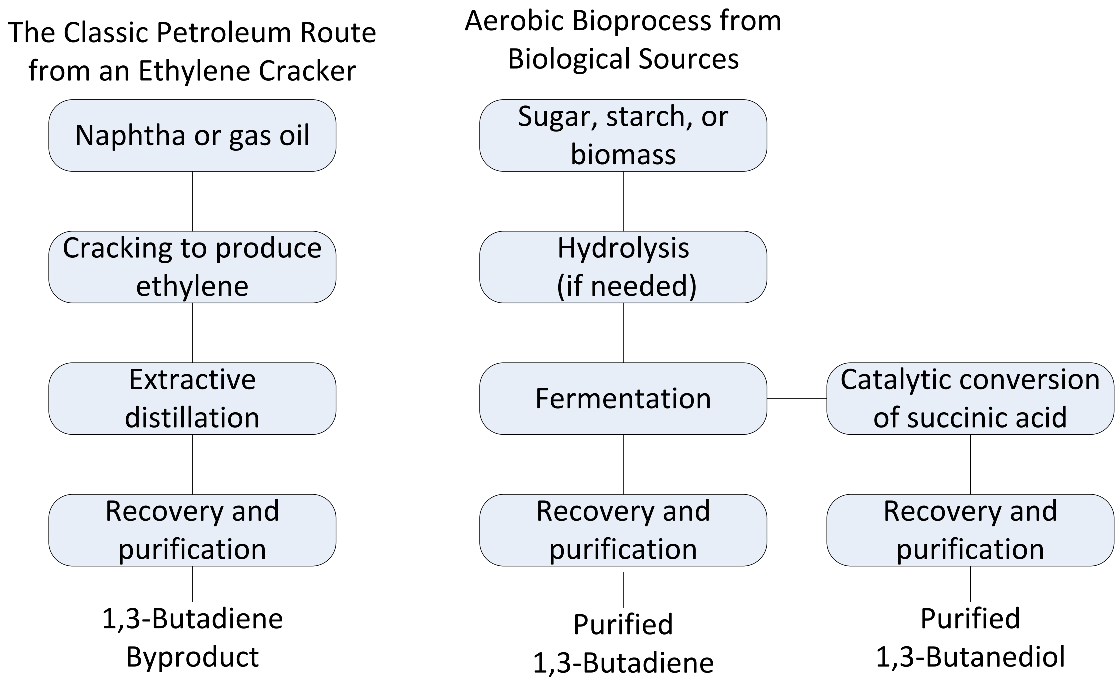

Figure 6. An overview of butadiene production pathways from petroleum and renewable feedstocks

Consumption and End Products

Total world consumption of butadiene in 2012 was about 10 million metric tons with growth expected to be around 1%–2% per year (Makshina et al. 2014). About 75% of the U.S.-produced butadiene is consumed in the production of styrene-butadiene rubber (SBR) that is used to make tires. Roughly 80% of the SBR market is for replacement tires, a market segment that affects both SBR and BD up through the supply chain; this has been significantly reduced in the past several years due to recessions in Asia and Europe. The rest of the butadiene produced in the United States goes toward making acrylonitrile-butadiene-styrene, which is used to produce plastics for appliances, electronics, automobiles, and piping for housing.

Price History and Volatility

As shown in Figure 7, butadiene spot prices are highly variable and have dropped over the past few years. This reduced cost is a result of decreased demand in the styrene-butadiene rubber market, in part due to low tire demands as a result of struggling global economies. In fact, U.S. contract prices of butadiene fell from an average of $3,200/metric ton in May 2012 to $1,740/metric ton in May 2013 (Yost 2013). Butadiene prices continued to fall in 2013 as the contract price in December 2013 was reported at $1,200/metric ton, down 28% from the December 2012 price of $1,676/metric ton (Dietrich 2014b). U.S. prices are expected to stay below $2,200/metric ton for 2014 barring any major supply outages (Dietrich 2014b).

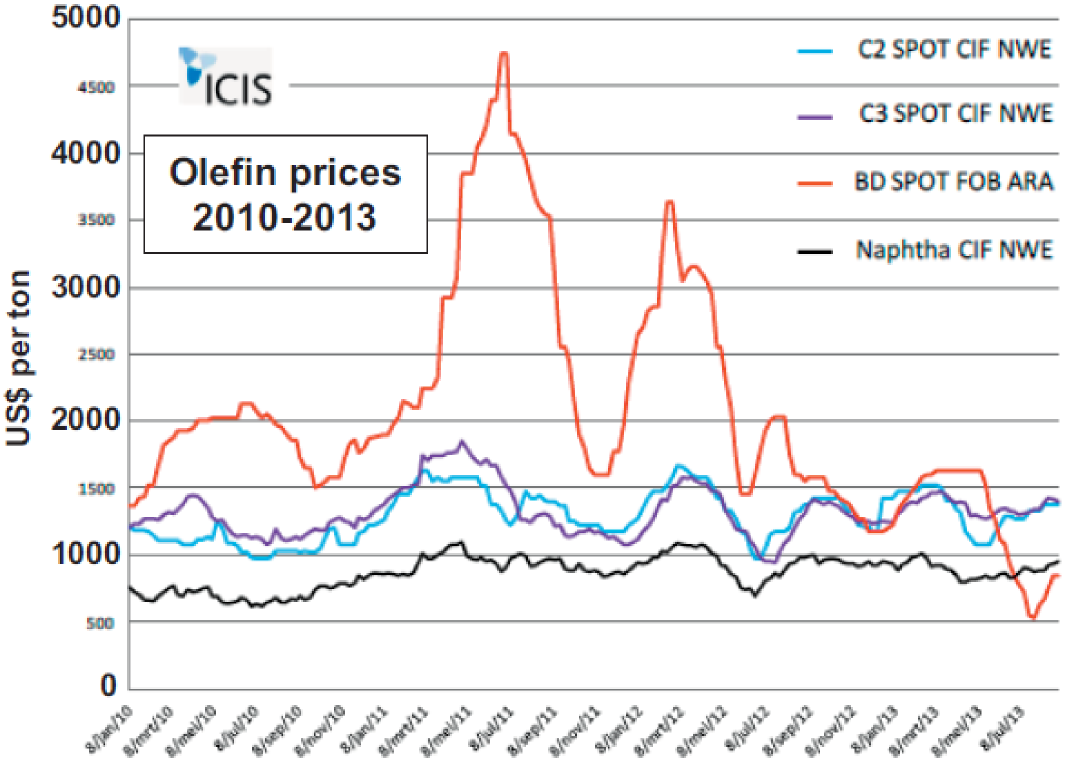

Figure 7. Butadiene spot price (Bender 2014)[2]

Current U.S. Market Status

The U.S. market for butadiene was strong between 1990 and 2000 and has since diminished due to new plants coming online in China and the Middle East and the shift to lighter feedstocks for ethylene production. The butadiene supply has remained tight since early 2000. The U.S. output of crude C4s has decreased by more than 20% since 2007 with the price of butadiene nearly doubling in this period (Lemos 2012, Bruijnincx and Weckhuysen 2013, Tullo 2013a). In fact, due to the high cost of raw materials, the cost of tires has risen by 64% since 2003 (Tullo 2013a).

The production of ethylene is expected to grow 20% by 2016 with the growth of C4s projected to increase only 10% due to the use of lighter feedstocks for ethylene production. Alternative technologies for the production of C4s are being pursued to overcome this tight supply. Specifically in the United States the conversion of butane is being pursued for butadiene production (Tullo 2013a). Biomass-derived butadiene is another promising alternative given the clear demand and projected increase in cost due to supply shortages.

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[2] Adopted from Bender, Michael. 2014. "An Overview of Industrial Processes for the Production of Olefins – C4 Hydrocarbons." *ChemBioEng Reviews* 1 (4):136-147. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Production from Renewable Sources

There are multiple production routes to bio-derived butadiene that are under development. Many of these routes are through biological upgrading of sugars to intermediates including butanediol (1,4 or 2,3), butenes (normal or iso-), or alcohols (ethanol or butanol). These intermediates are converted catalytically to butadiene. A direct route for the production of butadiene via the fermentation of sugars is also being pursued, although this direct process is more complex and incurs increased capital and operating costs and lower overall yields.

Several companies have reported the direct production of butadiene from renewable sources. Genomatica has reported producing pounds of renewable butadiene via direct fermentation of sugars. In 2013, they signed agreements with Braskem and Versalis. The company website notes that "Braskem anticipates funding Genomatica's development work; will allocate Braskem R&D resources; and fund the construction of pilot and demonstration-scale plants" (Genomatica 2014). Global Bioenergies has partnered with Synthos, which is a manufacturer of polybutadiene rubber, styrene-butadiene rubber, and latex (Lane 2014e). A goal of Global Bioenergies is to scale up direct production of butadiene from R&D to pilot scale by 2013 (Lane 2014e).

INVISTA, a nylon producer, is currently working with several firms to develop routes for bio-butadiene production. Partnerships between INVISTA and Arzeda have been announced for the production of renewable butadiene via the fermentation of sugars. INVISTA is also collaborating with the United Kingdom's Centre for Process Innovation to develop a direct production of butadiene from the fermentation of waste gases. In addition, INVISTA is working with LanzaTech to utilize syngas fermentation to 2,3-butanediol with further catalytic conversion to butadiene (Corp. 2014, Bomgardner 2012, 2013d) .

Cobalt Technologies has successfully demonstrated the fermentation of 1-butanol at the 100,000-L scale. Cobalt is working to convert butanol to butadiene with two unidentified Asian chemical producers, with a goal to build a commercial-scale facility in Asia (Bomgardner 2013b).

Finally, one of the larger funded efforts for the production of renewable butadiene that includes government support is a collaboration between the tire manufacturer Michelin, the catalyst and technology supplier Axens, and the public sector research organization IFP Energies nouvelles. This eight-year effort, which was announced in 2013, has a $70 million budget with $20 million in support from the French government (Bomgardner 2013e). This project focuses on the production of butadiene via bio-ethanol. The bio-ethanol is supplied from the French agribusiness firm Tereos (Makshina et al. 2014, Bomgardner 2013d).

Data Gaps

No data is available for bio-butadiene capital, operating, and product costs. A few detailed reviews have been developed recently by academics and Nexant for the USDA (Makshina et al. 2014, Nexant 2014b).

Market Forces/Drivers: Why this Bioproduct?

Michelin is a key market champion for bio-butadiene as they have strong interest in producing tires made with renewable materials. Further, international chemical companies are investigating routes toward replacing petroleum-derived butadiene with bio-derived butadiene, including Braskem, INVISTA, Synthos, and Versalis.

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

Many of the producers of bio-derived butadiene are also pursuing other routes for biofuels production, including LanzaTech and Genomatica. The major investors in these technologies, however, are traditional chemical producers such as Braskem and INVISTA.

Butanediol (1,4-)

1,4-butanediol, as shown in Figure 8, is a four carbon (C4) primary alcohol that is a building block for the production of polymers, solvents, and specialty chemicals. Current demand for BDO is just under 2 million metric tons per year. With this large market, and with market champions including Nike and INVISTA demanding renewable sources for the production of polymers, bio-derived BDO is being produced on a commercial scale utilizing commodity sugars by BASF. Genomatica has led efforts to develop technology to directly produced BDO and, with support from the DOE, the company has successfully demonstrated an integrated process utilizing a range of lignocellulosic sugars that has commercialization potential. Another promising conversion strategy currently being scaled-up is the catalytic conversion of succinic acid to BDO.

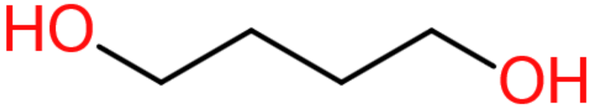

Figure 8. The chemical structure of 1,4-butanediol ($C_4H_{10}O_2$)

Production from Petroleum

There are a number of pathways for the production of BDO from petroleum including the Reppe process involving conversion of acetylene and formaldehyde, the butadiene-acetic acid process, oxidation of propylene to BDO, the Davy process which converts maleic anhydride, and the dichlorobutene process (Figure 9). The primary route for the production of BDO in the United States and Western Europe is the Reppe process. This process was initially developed in the 1930s by BASF and is a two-stage process where formaldehyde and acetylene are first reacted to form 1,4-butynediol that is then hydrogenated in the second stage to produce BDO. Typical yields of the process are around 90% of theoretical. The other commonly utilized process is the Davy process where maleic anhydride is initially esterified with ethanol and then hydrogenated to diethyl succinate and eventually BDO. Coproducts in the process include THF and gamma-butyrolactone (GBL), which allows for flexibility in the process economics when producing a range of commodity products (Nexant 2014a, Pitches 2013, Sampat 2013).

The largest producers of BDO include BASF, Dairen Chemical Corp., LyondellBasell, Ashland (formerly ISP), and Xinjiang Markor Chemical Industry; these companies produced more than 55% of the world’s BDO capacity in 2012 (Pitches 2013). In the United States, BDO is manufactured by BASF, INVISTA, Ashland, and LyondellBasell. Roughly 50%–80% of the U.S. BDO production fulfills captive demand as each of these companies are forward integrated to produce higher value downstream products including THF and GBL (Kirschner 2009). However, as of 2012, the world’s primary capacity for BDO was concentrated in Asia, with the bulk of the processes located in China. Projections are that China’s capacity for BDO will more than double in the next few years; however, capacity has been greater than actual demand and many of China's producers have production rates of 60% or lower (Sampat 2013, Pitches 2013).

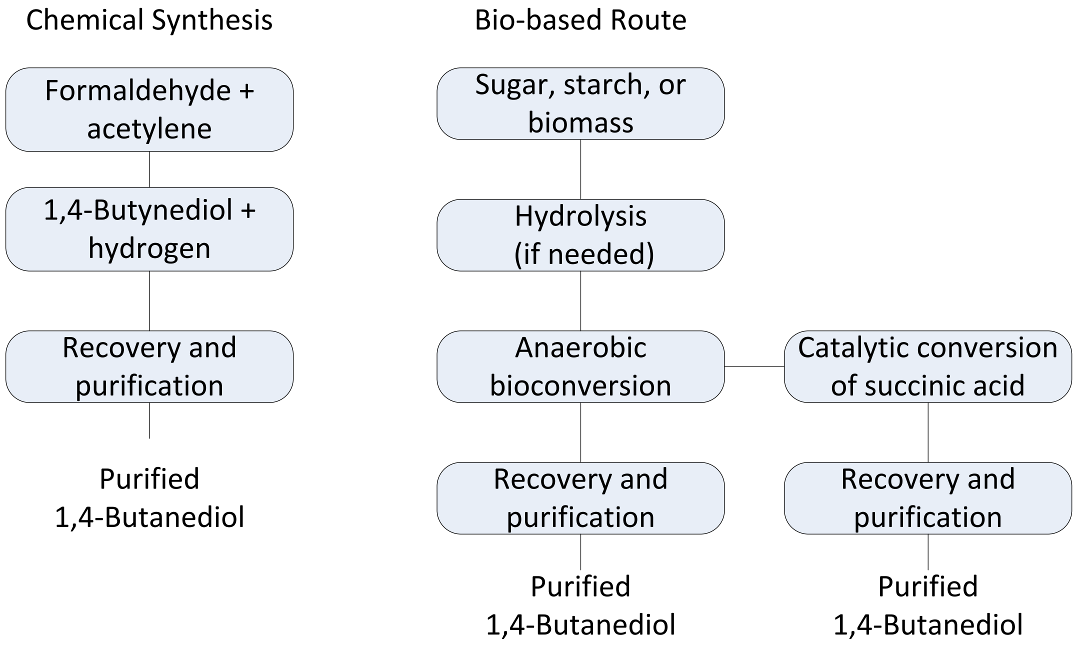

Figure 9. An overview of butanediol production pathways from petroleum and renewable feedstocks

Consumption and End Products

BDO is used as a chemical intermediate in the production of polymers, solvents, and specialty chemicals. About 45% of the world's BDO is converted to THF, which is then used as a monomer for the production of polytetramethylene ether glycol. This polymer is a component of spandex, urethane elastomers, and copolyester ethers (Pitches 2013). Approximately 25% of the world's BDO is reacted with terephthalic acid to produce polybutylene terephthalate (PBT). This strong and highly crystalline synthetic resin has properties desirable for injection molding (Sampat 2013). The next largest markets for BDO are for the production of GBL used as a solvent, a solvent precursor (in particular for N-methylpyrrollidone), and as an intermediate in the synthesis of herbicides (Kirschner 2009).

Price History and Volatility

The world BDO market is mostly captive (about two-thirds) with about half of the remaining available BDO market being held by long-term contracts (Sampat 2013, Kirschner 2009, ICIS 2013). Due to these defined markets, public pricing information for BDO is limited. Recent reports have indicated that prices of BDO in 2012 were the highest they have been over the last decade and have since declined over the last few years. U.S. BDO prices have dropped from the high in 2012 (about $3,500/short ton) to current prices reported around $3,000/metric ton (Martin 2014, Chem-Net Facts 2013). Markets in Asia and Europe have seen a larger decline in prices since 2012 and these prices are highly dependent on the Asian market. In recent years, the

U.S. supply has been very tight but imports may have a larger effect as more BDO processes come online in China. Imports have had minimal influence on U.S. markets thus far, as many experts have noted that Asian producers are not ready to bring material to the United States because logistical and permitting challenges are major barriers (Martin 2014).

Current U.S. Market Status

The projected growth of BDO in the United States is about 1% [3]. BASF, which owns and operates the largest BDO plant in the United States located in Geismar, Louisiana, is planning to expand production by 10% to help support growth in the company's downstream growth in polymer production (McCoy 2015a). Aside from the Ashland plant in Ohio, all BDO processes in the United States are located near the Gulf Coast, which can be impacted by hurricanes in the Gulf of Mexico. This has recently impacted BDO production with a number of operations temporarily shut down due to power outages (Balboa 2012).

Production from Renewable Sources

There are two primary routes for the production of BDO from renewable resources, namely direct fermentation and catalytic upgrading of fermentation intermediates.

Genomatica has been the leader in direct fermentation of sugar to BDO. In 2008, Genomatica announced a fermentation route to BDO using the biological conversion of commodity sugars with *Escherichia coli* (Bomgardner 2013a). In 2011, Genomatica developed an integrated pilot-scale demonstration of the process. By 2013, the company, with partner DuPont Tate & Lyle, demonstrated the first commercial production of biologically derived BDO by making more than 5 million pounds of BDO in a five-week campaign (Genomatica 2015a). In 2013, BASF had licensed the Genomatica technology and by December of that year had announced the production of commercial BDO (Bomgardner 2014a). BASF has since utilized renewable BDO to produce renewable polymers, as well as provided these renewable feedstocks to other polymer producers (Tullo 2013c). In 2015, Genomatica and Cargill announced the beginning of a collaboration to support the acceleration of bio-based manufacturing for BDO production, for example, through the co-location of a Genomatica BDO plant with a Cargill process facility (Bomgardner 2015b).

As highlighted in the succinic acid section of this report, the other route toward the production of bio-based BDO is by the catalytic upgrading of the fermentation product succinic acid. With the large amount of succinic acid that will soon be available in the marketplace, both Myriant and BioAmber are working with a number of catalyst companies and collaborators to develop routes toward the production of BDO. BioAmber, for example, plans to build a 100,000 metric ton per year BDO plant in North America with a targeted opening in 2017. This project is being funded, in part, by Vinmar International through a 15-year agreement signed with BioAmber under which the chemical distributor has agreed to invest in the plant and buy its output (McCoy 2015b).

Data Gaps

Biologically-derived BDO is currently produced at a commercial scale by Genomatica and BASF from commodity sugars. The development of this process utilizing lignocellulosic sugars has been pursued by Genomatica through a DOE grant. As highlighted in the final project report, there are a number of challenges that must to be overcome for the production of BDO from lignocellulosic sugars to be commercially viable; namely, engineering and improving *E. coli* strains that can not only utilize both C5 and C6 sugars in hydrolysates, but also targeting production toward desired products. For an integrated process, project results achieved titers that exceeded 120 grams per liter and productivities of greater than 3.1 grams per liter per hour on lignocellulosic sugars. While the company reports that they have achieved significantly better results with commodity sugar feedstocks, the engineering efforts have allowed the company to demonstrate feedstock flexibility. Further, the results of the project allowed for an integrated approach to the commercial design with key feedstock parameters, including sugar concentration and impurity allowances, to be identified not only for the organism development but also economic viability of the downstream recovery process.

Market Forces/Drivers: Why this Bioproduct?

The current BDO market is roughly 2 million metric tons per year. Similar to other C4 chemicals produced from petroleum, current low-cost production of ethylene by shale gas has reduced production of BDO while market demand has risen. Further, demand for renewable fibers has been supported by consumer demand. Market champions for bio-based BDO include INVISTA, owner of the LYCRA brand and one of the world’s largest integrated polymer and fiber producers. In 2014, the company announced the production of a new bio-derived LYCRA spandex fiber available globally for use in apparel fabrics with approximately 70% by weight from renewable resources derived from corn. The new fabric is to support INVISTA’s Planet Agenda to work toward reducing the company’s environmental footprint by conserving resources, reducing emissions, and eliminating waste at the company’s manufacturing plants. These efforts also align with the goals of Nike, which is developing brand lines, such as Considered, that utilize renewable resources. This market pull is developing demand for renewable products and helping to expand the commercialization for a drop-in BDO replacement (INVISTA 2014, Schilling 2010).

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

As highlighted previously, DOE has supported the expansion of the Genomatica BDO process to utilize lignocellulosic sugars per a grant funded from 2011–2014. As recently highlighted by Christophe Schilling, CEO of Genomatica, “Genomatica’s success with biomass is another step toward providing the industry with ‘best-fit’ feedstock flexibility… We are pleased to publish the hard data to support our innovation claims, and show that as biomass sugars are produced that meet quality and cost specifications, our technologies are ready to convert those sugars into polymer grade chemicals” (McCoy 2015b).

The project highlighted key metrics required for the production of chemicals from biomass-derived sugar considering a wide range of pretreatment technologies. Lessons learned in this study about the utilization of biomass-derived sugars and the engineering of metabolic pathways can be leveraged to improve production of not only chemicals but also fuels (INVISTA 2014).

Ethyl Lactate

Ethyl lactate (Figure 10) is a biodegradable solvent produced by the esterification of ethanol and lactic acid. The primary use for ethyl lactate is as an industrial solvent, as its properties and performance has been found to meet or exceed those of traditional solvents like toluene, methyl ethyl ketone, and N-methyl-pyrrolidone in many applications (Pereira, Silva, and Rodrigues 2011).It has been the subject of hundreds of journal articles and has attracted attention because both of the starting materials used to make ethyl lactate, lactic acid and ethanol, have the potential to be made from lignocellulosic sugars (Pereira, Silva, and Rodrigues 2011).

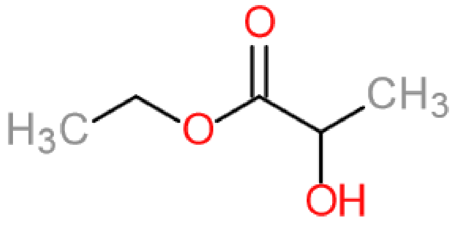

Figure 10. The chemical structure of ethyl lactate ($C_5H_{10}O_3$)

Production from Petroleum

Ethyl lactate can theoretically be produced from petroleum, but based on current information, no synthetic ethyl lactate is on the market. Synthetic lactic acid, prepared as described elsewhere in this report, and synthetic ethanol from ethylene or acetic acid could be starting materials.

Consumption and End Products

Ethyl lactate is primarily used as a functional replacement for solvents in metal cleaning and as a dispersant in pharmaceuticals. Testing at Argonne National Laboratory showed that a commercial ethyl lactate solvent was a preferred choice for degreasing machine parts due to its performance and recyclability (Wildes 2001). It has also been traditionally used as a flavor compound in food applications. It has desirable properties for use as a coating and resin solvent including a high boiling point, low vapor pressure, and low surface tension.

Price History and Volatility

The estimated demand for all solvents in the United States is approximately 5 million metric tons annually with prices ranging from \$2–\$4/kg. Ethyl lactate prices have been somewhat higher at \$3–\$4/kg with the expectation that prices will drop due to the economies of scale and process or supply chain improvements that are on par with some petroleum-derived solvents selling at \$2/kg (Pereira, Silva, and Rodrigues 2011, de Jong et al. 2012a, Watkins 2002).

Current U.S. Market Status

Three companies—ADM, Galactic, and Cargill Dow—have U.S. ethyl lactate production facilities. Galactic operates globally; their U.S. facility is in Milwaukee, Wisconsin, and as of 2011, has a capacity of 15,000 tons per year (Galactic 2014). ADM operates multiple ethanol plants in the United States with an annual production of 1.8 billion gallons (ADM 2014a). They also produce lactic acid; production is assumed to be associated with one or more of their many corn mills. Cargill Dow produces ethyl lactate at their facility in Blair, Nebraska. Other global firms mentioned in the lactic acid section of this report also have the capability to produce ethyl lactate, including polylactic acid-focused companies like Purac (PURAC 2014). Another company, VertecBio, produced the solvent used in the Argonne work mentioned above (Wildes 2001, Watkins 2002). VertecBio is a formulator and reseller rather than a primary producer of ethanol and lactic acid (VertecBio 2014).

Production from Renewable Sources

It appears that all ethyl lactate is currently produced from ethanol and lactic acid made from renewable sources (e.g., starch or sugar). Ethyl lactate has gained traction as a functional replacement for petroleum solvents in a number of applications. Ethanol is a useful raw material in the chemicals industry and has seen tremendous growth for use as a blending component in transportation fuel (EIA 2014). Similarly, lactic acid has seen growth driven by demands in the chemical industry for use as a polymer feedstock (described elsewhere in this report). There are a number of patented processes for the synthesis of ethyl lactate. Typically the esterification reaction is carried out to equilibrium and the ethyl lactate product is removed by distillation. Excess ethanol can be added to shift the equilibrium toward greater ethyl lactate conversion and an acid catalyst may be added. Reactive distillation and membrane-based processes have been reported that can improve product yield and purity (Pereira, Silva, and Rodrigues 2011). With the recent commissioning of commercial-scale cellulosic ethanol plants in the United States, products like ethyl lactate move a step closer to being produced from biomass feedstocks (POET 2014b).

Data Gaps

Some disagreement exists in the literature regarding the production volumes of ethyl lactate versus the availability of lactic acid on the market. Each year, there are billions of gallons of ethanol available in the United States alone, suggesting that ethyl lactate production is not limited by ethanol availability. However, global lactic acid production was estimated to be 300,000–400,000 tons in 2013 (Harmsen, Hackmann, and Bos 2014, de Guzman 2012e), most of which was consumed in food or polymer applications. No data was available from IHS on ethyl lactate for comparison. A different source, IEA Bioenergy Task 42, suggested that the global production capacity of ethyl lactate was 1.2 million metric tons (de Jong et al. 2012a). The two sources used data that was a decade apart: 2012 for IHS and no later than 2003 for the IEA report (Weissermel and Arpe 2003). IHS reported global lactic acid production in 2003 to be about half of the 2012 output. One possible explanation is that lactic acid used for ethyl lactate production was consumed directly on site (i.e., was never sold on the market) and was therefore not counted in the IHS data. The other data gaps for ethyl lactate production will be similar to that for the scale-up of lactic acid and ethanol from lignocellulose.

Market Forces/Drivers: Why this Bioproduct?

There is market pull for ethyl lactate because of its desirable performance and properties as a green solvent. Ethyl lactate is biodegradable, non-corrosive, non-carcinogenic, low in volatile organic compounds, and it is inexpensive to recover and recycle (Wildes 2001, Pereira, Silva, and Rodrigues 2011).

It was listed as part of the EPA’s SNAP as a solvent that meets the ozone protection provisions of the Clean Air Act (EPA 2015b, EIA 2014). It has been used in industrial applications to replace volatile organic petroleum-derived compounds. Because of its low toxicity, it has found use in food, pharmaceutical, and personal care applications.

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

Ethyl lactate is a well-established, commercially proven green solvent, with increasing acceptance in the marketplace. Its starting materials, ethanol and lactic acid, have high potential to be produced from lignocellulose. Ethyl lactate is relatively simple to produce and may present a good opportunity as a value-added coproduct from biorefineries.

Fatty Alcohols

Fatty alcohols, also called detergent alcohols, are linear alcohols of 12 or more carbons (Figure 11), used primarily to produce anionic and non-ionic surfactants for household cleaners, personal care products, and industrial applications. Shorter chain alcohols, in contrast, are used most often in plasticizers. Fatty alcohols accounted for 11% of current bio-based chemicals in commercial production (IHS 2014a). Fatty alcohols are derivatized by ethoxylation, sulfation, or sulfonation before use. They can be produced from tallow, vegetable oils, or petroleum. Each of these classes of feedstocks can be substituted for one another in many applications (i.e., as functional replacements) and the market for detergent alcohols is price sensitive. This has led to rapid geographic shifts in detergent alcohol production and an overall move to price-competitive naturally-derived feedstocks. Fatty alcohols have the potential to be produced from renewable sources by autotrophic and heterotrophic algae or by microbial fermentation of carbohydrates.

Figure 11. The chemical structure of palmityl alcohol ($C_{16}H_{34}O$), a representative, commercially important fatty alcohol

Production from Petroleum

Detergent alcohols from ethylene are branched while natural oils produce linear alcohols; therefore, they generally do not compete for the same applications, although there is some overlap. Shell and Sasol are the leading global producers of synthetic detergent alcohols. Almost all of the remaining production is from natural oils.

Benzene, n-paraffins, syngas, and ethylene have been used as feedstocks to produce detergent alcohols. Synthesis proceeds through a linear alpha-olefin or linear alkyl benzene intermediate. The commonly used oxo process (hydroformylation) for the synthesis of detergent alcohols from ethylene is highlighted in Figure 12. Alpha olefins synthesized from ethylene are reacted with syngas in the presence of a catalyst to form a mixture of linear and branched aldehydes. The aldehydes are reduced to a mixture of linear and branched detergent alcohols. Shell Chemicals has a modified oxo process in which the aldehyde formation and hydrogenation to alcohols takes place in a single reactor in the presence of proprietary catalysts. Other approaches like the Ziegler and Alfol processes produce trialkyl aluminum intermediates prior to oxidation to alcohols. A number of other technologies have been used, but they have been displaced by processes that use natural oils as a starting material due to feedstock prices.

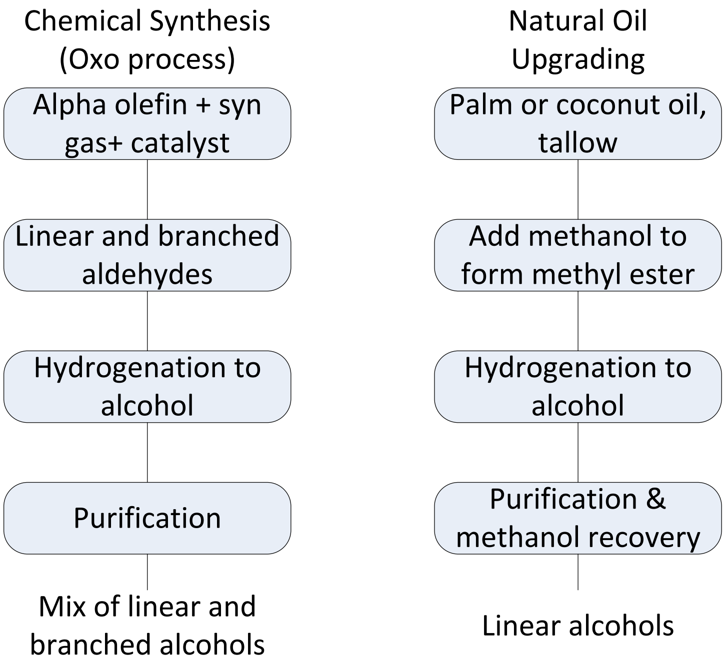

Figure 12. An overview of detergent alcohol production pathways from petroleum and biomass

Consumption and End Products

Detergent alcohols are precursors to surfactants used in a variety of consumer and industrial applications. Household detergents for laundry, dishwashing, and other cleaning products account for more than half of the market for detergent alcohols. Personal care products make up nearly a quarter of the demand. There has been a transition to renewable sources for many of these consumer-touching products and the trend to source detergent alcohols from vegetable oils has followed. The remainder of the demand is in the industrial sector including diverse uses in plastics processing, oil additives, metalworking fluids, wastewater treatment, and oil field chemicals.

Price History

The raw material source (petroleum or vegetable oil) of the detergent alcohol affects its price. The price volatility is dependent on the price of the feedstock in all cases. However, supply has outstripped demand and many processors are struggling to recoup costs since the recession. Price estimates have been in the $2–$3/kg range depending on the source, carbon chain length, and application (IHS 2015a, ICIS 2012c).

Current U.S. Market Status

Procter & Gamble and BASF are the U.S. leaders in natural fatty alcohol production. Shell and Sasol are the leading producers of synthetic fatty alcohols. Production in the United States has followed three macro trends over the last few decades. Low priced vegetable oil in the late 1990s led to decreased tallow-based production in the United States, Europe, and Japan. Then Shell and Sasol led a U.S. resurgence of ethylene-based production in the early 2000s. This competed with vegetable oils as global production of biodiesel increased. The United States now has excess capacity and has been a net exporter of alcohols. As with other products, most of the growth will occur in emerging markets.

Production from Renewable Sources

Fatty alcohols are classified based on the source of the raw material inputs and may be natural or synthetic. Synthetic alcohols are sourced from petrochemicals. Natural alcohols are sourced from plant or animal fats and oils (i.e., lipids). The choice of raw material is often determined by the raw material cost. Increased supplies of inexpensive coconut and palm oils in Southeast Asia have led to an increased supply of natural fatty alcohols. However, there are a number of rising environmental concerns, including land use change, from increased production of these oils

The primary route to fatty alcohols from natural sources is through the reduction of methyl esters. Triglycerides (i.e., fats or oils) are treated with excess methanol in the presence of a strong base like sodium methoxide (CH_3ONa) to produce biodiesel. Fatty acids are hydrolyzed from the glycerol backbone and esterified with methanol.. There is oversupply in the glycerol market, discussed in the Glycerin section of this document, making it difficult generate value from this byproduct. A slipstream of the methyl esters are recovered by distillation and hydrogenated to fatty alcohols. Hydrogenation takes place at very high pressures (200 atm) using a copper chromite catalyst and hydrogen. Methanol is recovered at this stage and recycled back into the process. Fatty alcohols are then further purified and fractionated by chain length.

LS9, Inc., has used genetically modified *E. coli* to produce $C_{10\text{–}18}$ fatty alcohols from sugar feedstock. LS9 commissioned a pilot-scale, 135,000-liter fermenter in Okeechobee, Florida, in 2012. The facility could produce 700–1,000 metric tons of fatty alcohols per year. LS9 planned to build a commercial facility in Brazil with fermentation capacity of 50,000 metric tons per year of detergent alcohols (Boswell 2014b). LS9 was interested in setting up multiple sites with a total production capacity amounting to 200,000–500,000 metric tons per year in the full-scale phase around 2018–2020. LS9 was sold to Renewable Energy Group in 2014 for $61.5MM (Wesoff 2014). It is unclear how this will impact the earlier investments in fatty alcohol production.

Codexis began producing fermentation derived fatty alcohol production at a 650-liter pilot facility in 2012 with plans to scale up to 60,000 tons per year in 2015 (ICIS 2012c). Similar to LS9, Codexis used bacteria to ferment sugars to fatty alcohols. In 2013, they partnered with Chemtex, an Italian engineering firm, to develop technology to produce cellulosic sugars for upgrading to fatty alcohols. By the end of 2013, Codexis had exited the production of fatty alcohols in order to pursue biocatalyst development (de Guzman 2013a).

The algae technology company Solazyme has partnered with Bunge in Brazil to produce 100,000 tons per year of oils for chemical and fuel applications including fatty alcohols. The Solazyme technology enables tailored composition and degree of saturation in their oil products. Tim Dummer, vice president commercialization at Solazyme, states that “control of both chemical and physical properties enables the production of oil mimetics, enhanced oil compositions, and novel oil compositions never previously commercially available” (ICIS 2012c).

Data Gaps

Microbial production of fatty alcohols, similar to the free fatty acid pathway described in the 2013 National Renewable Energy Laboratory (NREL) design report (Davis et al. 2013), requires that oxygen be supplied to the microbes. These aerobic bioprocesses have two challenges. First, large compressors are needed to pump air at a high flow rate into bioreactors. This results in high capital expenditures for the aerobic fermentation vessels and for the compressors themselves. Operating costs are higher due to the increased power demand to drive the compressors. Second, the carbon yield from sugars to fatty alcohols is impacted by microbial metabolism. Fatty alcohol syntheses proceed through central metabolism from sugars to pyruvate, to acetyl-CoA intermediates prior to fatty alcohol synthesis. Two molecules of CO_2 are produced from the metabolism of glucose to two molecules of acetyl-CoA; therefore, a minimum of one-third of the carbon in a C6 sugar like glucose is lost to CO_2 during fatty alcohol production.

Market Forces/Drivers: Why this Bioproduct?

The EPA in the United States and Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) in the European Union have regulations and programs that encourage the use of low toxicity (to aquatic life), biodegradable surfactants (EPA 2014a, European Commission 2014). Natural fatty alcohols, including those from algae or microbes, are more likely to meet these criteria and would likely be on par with plant-derived fatty alcohols.

There is excess fatty alcohol production in the United States and global feedstock production has shifted to lower-cost natural sources like palm and coconut oils. These factors will put downward pressure on prices in the short term. As global demand increases, new capacity will have to come online. There is an opportunity for algal- or biomass-derived fatty alcohols to meet a portion of that demand.

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

Detergent alcohols would be a likely fit as a coproduct from an algal or biochemical-based biorefinery producing fatty acids for upgrading to hydrocarbons. This concept would enable a flexible product mix, whereby production could be shifted between the detergent alcohol market and hydrocarbon market as price fluctuates for each product.

Furfural

Furfural (Figure 13) is a heterocyclic aldehyde, produced by the dehydration of xylose, a monosaccharide often found in large quantities in the hemicellulose fraction of lignocellulosic biomass. In theory, any material containing a large amount of pentose (five carbon) sugars, arabinose and xylose, can serve as a raw material for furfural production (Cai et al. 2014). Most furfural is converted to furfuryl alcohol (FA), which is used for the production of foundry resins. The anti-corrosion properties of FA make it useful in the manufacture of furan fiber-reinforced plastics for piping. Furfural has a broad spectrum of industrial applications, such as the production of plastics, pharmaceuticals, agro-chemical products, and non-petroleum-derived chemicals (Mamman et al. 2008). Furfural is not produced from petroleum or fossil fuels, therefore current production methods from biomass do not displace production from petroleum. However, recent research has reported a furfural-to-distillate fuel pathway that could potentially make furfural derivatives a drop-in replacement for petroleum-derived distillate fuels (jet and diesel). Furfural demand in the U.S. is not expected to grow significantly, therefore the primary market driver for the production of furfural may be conversion to jet and diesel fuel blendstocks.

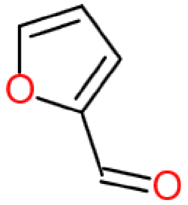

Figure 13. The chemical structure of furfural ($C_5H_4O_2$)

Production from Petroleum

No references could be found that report furfural production from petroleum. According to Mamman et al., there is no synthetic route for the production of furfural (Mamman et al. 2008).

Consumption and End Products

Industrial furfural production started in 1921 by the Quaker Oats Company, using oat hulls, corn cobs, and sugar cane bagasse. Current global production of furfural is around 270,000 metric tons/year, with three nations accounting for 90% of production. China produces the greatest amount, accounting for about 70% of global production. The Dominican Republic and South Africa are the second and third largest producers, respectively (Yan et al. 2014). Most other sources report production levels consistent with 270,000 metric tons/year (Agirrezabal-Telleria, Gandarias, and Arias 2014), except Mao et al. (Mao et al. 2012), which reports global production of 635,000 metric tons/year, although this is by far the highest estimate found in literature. Historic and projected furfural global demand is presented in Figure 14 (DalinYebo 2014a).

Furfural demand generally tracks with economic growth and thus suffered due to the recent global economic crises, although potential new applications and a growing preference for environmentally friendly products provides a basis for continued market growth (DalinYebo 2014a).

Figure 14. Past, present, and future global furfural market scenario (DalinYebo 2014a)[3]

Furfural is used directly as a solvent to dissolve aromatics and other unsaturated olefins. Oil companies use furfural as a selective solvent in the refining of lubricating oils. Aromatics, polar components, and mercaptans are removed from petroleum by furfural extraction (International Furan Chemicals 2014a). Furfural is a platform chemical derived from renewable biomass feedstocks. It is the precursor for many furan-based chemicals and feedstocks (Yan et al. 2014), including methylfuran, furfuryl alcohol, tetrahydrofurfural alcohol, tetrahydrofuran, methyltetrahydrofuran, dihydropyran, and furoic acid (Cai et al. 2014).

Most furfural is catalytically hydrogenated to value-added products, several of which are described in Yan et al. (Yan et al. 2014) and summarized in Table 5 and Figure 15. Production of jet fuel from furfural has been explored by Bond et al. (Bond et al. 2014). Furfural produced from the hemicellulose fraction of red maple wood was converted to a mixture of linear and branched alkanes with carbon numbers ranging from C_7 to C_{31} in a three-step process. First furfural is condensed with acetone under basic conditions to produce a conjugated C_{13} compound, furfural-acetone-furfural (FAF). Second, FAF is hydrogenated over a noble metal catalyst to improve thermal stability. Third, the hydrogenated product is processed with hydrogen co-feed over bifunctional catalysts to eliminate the remaining oxygen and isomerize the product to linear and branched alkanes. A techno-economic analysis (TEA) estimated the minimum selling price of $4.75 per gallon (approximately $1.60/kg) for the final distillate products (naphtha, jet and diesel fuels), but no economic analysis was conducted exclusively on the furfural-to-alkanes step. For comparison, the jet fuel spot price is about $3.00 per gallon when West Texas Intermediate crude is $100/bbl (based on EIA historical data). Making liquid

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[3] Reproduced with permission from DalinYebo.

transportation fuels from furfural is challenging due to generally lower value of fuels versus chemicals however it potential opens up a larger market opportunity. The deoxygenation required for conversion to fuels inherently results in yield loss on a mass basis, whereas conversion to chemicals may not require deoxygenation.

Table 5. Chemicals and Products Derived from Furfural

End Use/Application	Notes
Furfuryl alcohol (FA)	It is estimated that about 62% (Yan et al. 2014) of furfural produced each year is converted to furfuryl alcohol, most of which is used for the production of foundry resins. The anti-corrosion properties of FA make it useful in the manufacture of furan fiber-reinforced plastics for piping. FA can also be converted to 1-pentanol, which is a solvent for coating DVDs (Yan et al. 2014).
Tetrahydrofurfuryl alcohol (THFA)	THFA is a "green" solvent used in agricultural applications, printing inks, and industrial and electronics cleaners. It can also be converted to 1,5-pentanediol, which is used as a plasticizer (Yan et al. 2014).
2-methylfuran (MF)	MF is used as a feedstock in the production of antimalarial drugs such as chloroquine. Also used to produce methylfurfural, nitrogen and sulfur heterocycles, and functionally substituted aliphatic compounds (Yan et al. 2014).
2-methyltetrahydrofuran (MTHF)	MTHF is a specialty solvent, used mainly as a substitute for tetrahydrofuran, due to its inverse solubility with water (solubility decreases with increasing temperature). MTHF can also be used in the manufacture of lithium electrodes (Yan et al. 2014) and as a component in alternative fuels, as it has an octane number of 87 (Huber, Iborra, and Corma 2006).
Furan	Furan often occurs as a side reaction during hydrogenation of furfural, but can be targeted through catalytic decarboxylation of furfural at high temperatures (Yan et al. 2014). It is used as a solvent as well as in the synthesis of furan-based compounds. It is converted to tetrahydrofuran by hydrogenation. Nitro-substituted furan derivatives are used as biocides or fungicides. Sulfur-substituted furan derivatives are used as flavoring agents (ChemicalAnd21.com 2014).
Tetrahydrofuran (THF)	Derived from furan via hydrogenation, THF is used as a solvent for many chromatography applications and as an ingredient in adhesives, PVC cements, vinyl films, and cellophane (Yan et al. 2014).
Cyclopentanone	A chemical intermediate, cyclopentanone is used in the production of pharmaceuticals, insecticides, and rubber chemicals (Yan et al. 2014).
Cyclopentanol	Cyclopentanol is used as a perfume and pharmaceutical solvent and as an intermediate chemical for dyes and pharmaceuticals (Yan et al. 2014).
Maleic Anhydride	The biggest single use of maleic anhydride is in the manufacture of unsaturated polyester resins, which are used in fiber-reinforced plastics and materials used in the boating, automotive, and construction industries. It is also used to make alkyl resins, which are used in paints and coatings (Bartek 2014, Alonso-Fagfflndez et al. 2012).

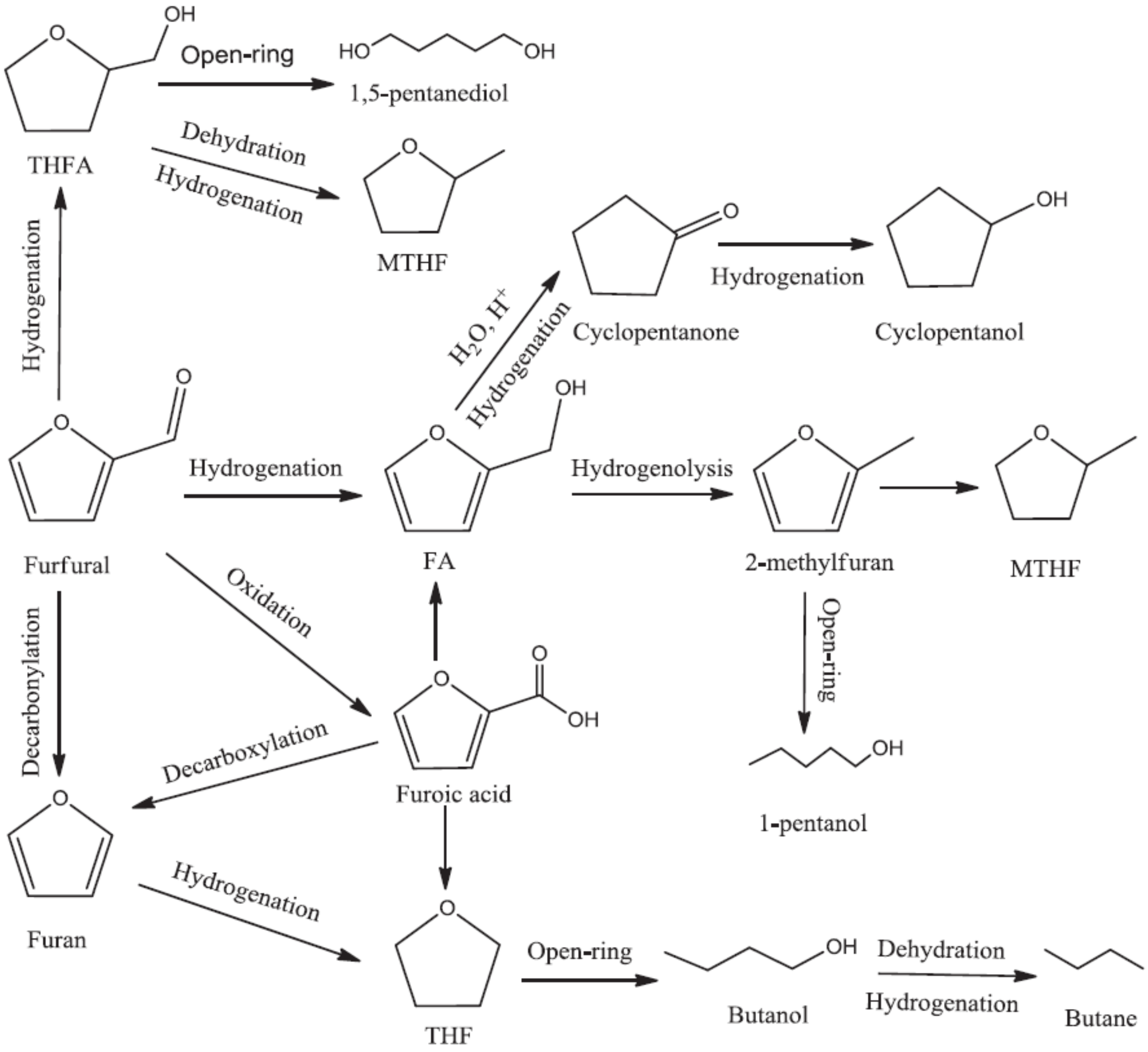

Figure 15. Conversion of furfural to value-added chemicals and biofuels (Yan et al. 2014)[4]

Price History and Volatility

In 2002, the market price of furfural was reported to be around $1,874/metric ton (Yan et al. 2014). In 2011, the reported price was around $2,200/metric ton (Yan et al. 2014, Mao et al. 2012). For 10 years, until 2009, furfural prices have remained relatively stable between $720 and $1,300/metric ton (DalinYebo 2014b) China has about 80% of the global furfural production capacity and consumes about 75% of it. Global furfural prices are driven by domestic Chinese issues such as droughts and floods, labour costs, feedstock availability and cost, and government policies (e.g., anti-pollution or finance) (DalinYebo 2014b). The price of corncobs has been the

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[4] Reprinted from *Renewable and Sustainable Energy Reviews*, 38, Kai Yan,Guosheng Wu,Todd Lafleur, Cody Jarvis, "Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals," 663-676. Copyright (2014), with permission from Elsevier.

most significant factor for production cost. Southeast Asian coal prices have also had an impact (DalinYebo 2014b). One report commented on future furfural prices, “It's complicated: Based on above price determinants and given the current economic outlook for 2014, we expect the prices to remain in a U.S. $1,540 to $1,650/metric ton FOB [free on board] price range” (DalinYebo 2014b).

Current U.S. Market Status

Furfural consumption will continue to be driven by demand for furfural alcohol, particularly in China where furfural alcohol, used for the production of foundry resins, continues to grow. In the United States and Western Europe furfural demand is forecast to grow only slightly, 1%–2% annually, due to limited foundry industry growth (DalinYebo 2014b). A review of the literature found no furfural production facilities operating in the United States and no plans to build new capacity. Harborchem, based in Cranford, New Jersey, claims to be the only U.S. importer of furfural and furfuryl alcohol. Harborchem’s furfural and furfuryl alcohol are produced by Illovo Sugar Limited of Durban, South Africa (Harborchem 2014).

Production from Renewable Sources

There is no synthetic route available for the production of furfural. It is exclusively produced from lignocellulosic biomass by dehydrating pentoses, usually xylose (Mamman et al. 2008). Furfural became available in quantities of several tons per month in 1922 from the Quaker Oats Company in Cedar Rapids, Iowa.

Furfural can be produced by one-stage or two-stage technologies. In the one-stage technology, pentosans are hydrolyzed into xylose and then dehydrated into furfural simultaneously. In the two-stage process, hydrolysis of pentosans occurs under mild conditions, followed by the dehydration of xylose into furfural. The two-stage process achieves higher furfural yield than the one-stage technology, and solid residue is less degraded and can be used for conversion to other chemicals in a subsequent step via fermentation (e.g., ethanol and phenols) (Sánchez et al. 2013). The process can also be batch or continuous (Agirrezabal-Telleria, Gandarias, and Arias 2014). The original Quaker Oats process employs aqueous sulfuric acid in batch mode at 177°C (350°F) to achieve a 40%–50% yield (Yan et al. 2014).

The finer details of commercial furfural production processes are not public knowledge, but Agirrezabal-Telleria et al. (Agirrezabal-Telleria, Gandarias, and Arias 2014) describes a process configuration commonly used in China. Corncobs are continuously fed to the reactor/digester. Sulfuric acid is also added continuously to make up 3–4 wt% of total slurry. The total slurry is fed to the reactor, which is directly heated with steam. The pentosan hydrolysis and pentose cyclodehydration reactions occur in the same vessel. Steam provides heat to the process and also strips furfural from the slurry. Furfural is usually recovered via azeotropic distillation, decanting, and further dehydration. The steam-to-product ratio is high, and the sulfuric acid remains in the solid residue, which is usually dumped (Agirrezabal-Telleria, Gandarias, and Arias 2014). This process is highlighted in Figure 16.

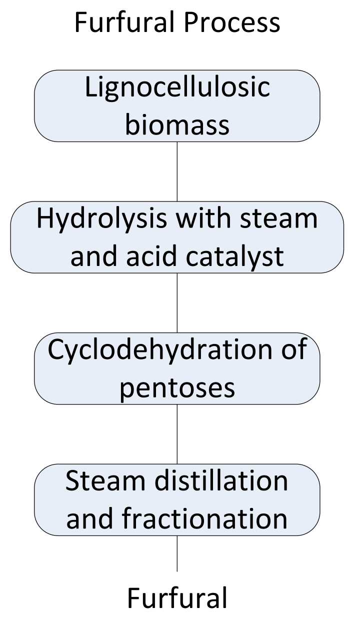

Figure 16. Production of furfural

Current production technology suffers from several deficiencies (Marcotullio 2013):

- Low yields, approximately 50% of theoretical
- High energy use, 20–50 tons of steam per ton of furfural product
- High sulfuric acid usage, roughly 20% of furfural output.

New production strategies have been under investigation, most using higher reaction temperatures and novel product recovery strategies, such as the SupraYield process, which operates at 240°C and incorporates *in situ* furfural recovery by flash decompression (Agirrezabal-Telleria, Gandarias, and Arias 2014).

Corncobs and bagasse from sugar cane are the major industrial feedstocks for furfural production (Hoydonckx 2008); therefore, lignocellulosic biomass is the primary feedstock for most of the current global production capacity. It should be clarified that furfural is made from the hemicellulose fraction of lignocellulosic biomass, not the cellulose or lignin fractions. In commercial operations the lignin and cellulosic residues are dried and used as fuel to provide steam to the facility.

The SupraYield process, developed by DalinYebo, employs orthophosphoric acid as a catalyst and *in situ* flash decompression for product recovery. The process achieved 80% yield at pilot-scale in South Africa. Successful pilot-scale operations led to a commercial facility in Australia owned by Proserpine Sugar. According to PSM Biorefinery (as quoted on the DalinYebo website): “Considering that this process relies on the physical properties of the components, and that these are not affected by the scale of the operation, there are no issues due to scaling up the

SupraYield process from pilot plant to full size." In 2009, Proserpine Sugar announced the first production of furfural from bagasse (DailinYebo 2014).

A new process to produce furfural and coproducts formic and acetic acid from waste aqueous hemicellulose solutions is presented by Xing et al. (Xing, Qi, and Huber 2011). In the process, furfural is produced in a two-step procedure consisting of the hydrolysis of xylose oligomers followed by the dehydration of xylose monomers and then extraction of the furfural into an organic solvent. The authors estimate this new approach requires 67% to 80% less energy than the current furfural production processes. An economic analysis indicates the new process can produce furfural for $366 per metric ton in 2009 dollars.

Data Gaps

The potential furfural yield for a typical feedstock can be expressed in terms of kg of furfural per metric ton of dry biomass. It is reported to be 220 kg/metric ton for corncobs, 170 kg/metric ton for bagasse, 160 kg/metric ton for cornstalks, 160 kg/ton for sunflower hulls, and 150–170 kg/metric ton for hardwoods (Mamman et al. 2008).

The theoretical furfural weight-basis yield is 72.7 wt% from pentosan and 64 wt% from pentose. The potential furfural production yield for each feedstock can be correlated to its average pentosan content: 22% for corncobs, 17% for bagasse, and 16% for cornstalks, sunflower hulls, and hardwood (Agirrezabal-Telleria, Gandarias, and Arias 2014). Other agricultural residue feedstocks, such as corn fiber, have been studied as well. Commercial yields around 50% of theoretical are most common, which is how yields are most often reported: actual yield divided by theoretical best possible yield based on the pentosan content on the feedstock.

Cost of production for furfural is not published by manufacturers, although Delft University of Technology estimates furfural can be produced for around U.S. $880/metric ton by an integrated process proposed in Marcotullio et al. (Marcotullio 2013).

One of the greatest challenges facing carbohydrate dehydration reactions to furanic aldehydes is the control of the secondary reactions leading to yield-loss reactions. Current research activities focus on using two main strategies: the use of heterogeneous selective acid-catalysts and the improvement of reaction systems (Agirrezabal-Telleria, Gandarias, and Arias 2014).

Currently, commercial production of furfural suffers from technological challenges and maintenance problems. Aqueous sulfuric acid is highly toxic, corrosive and difficult to handle. It must either be recovered for its reuse or neutralized, which creates a disposal problem. Modifications or improvements to make the overall process devoid of all these shortcomings are highly desirable for the sustainable growth of furan-based chemical industries. Such improvements in these commercial processes can be brought about only when more efficient, more environmentally friendly solid acid catalysts are used (Mamman et al. 2008). Advances cited in the literature as necessary for further commercialization of furanic aldehydes, such as furfural, include improved one-step synthesis of furfural directly from biomass-derived carbohydrates or lignocellulosic biomass; high-efficiency and energy-efficient separation and purification technologies such as membrane separation and supercritical carbon dioxide extraction technologies for desired products; and a complete techno-economic evaluation of the processes for the production of furanic aldehydes and related fuels and chemicals (Hu et al. 2012).

Market Forces/Drivers: Why this Bioproduct?

As stated previously, Chinese demand has absorbed most of China's production capacity, therefore China has begun importing furfural and demand in China is expected to grow steadily. As there are no plans to build production capacity in the United States, increased demand will most likely be met with increased production in China, South Africa, or the Dominican Republic. The result may be steady increases in furfural prices. U.S. demand is expected to grow only slightly, although 100% of furfural used in the United States is imported. This presents a domestic coproduct opportunity for U.S. biorefineries if they can leverage inexpensive agricultural residues already on site and employ the most recent advances in furfural production technology.

Recent advances in furfural production technology (Agirrezabal-Telleria, Gandarias, and Arias 2014, Bozell and Petersen 2010, Marcotullio 2013) report impressive improvements in yield, reduced energy use, and more environmentally friendly catalyst options, although detailed techno-economic analyses incorporating these advances have not been conducted to evaluate the economic potential of furfural production in the United States.. Furfural yield of current production facilities is reported to be about 50%, whereas modified processes such as the Biofine and Vedernikov processes, report 70%–75% furfural yield (Cai et al. 2014). At the very least, recent research advances at the laboratory scale may justify revisiting furfural with a detailed TEA. At crude oil prices of $100 per barrel, the cost of furfural production must be reduced by 46% for improvements in furfural derivatives to compete with petroleum-based products (Cai et al. 2014).

In recent laboratory experiments, furfural has been converted to jet and diesel blendstocks, which is convenient as demand for distillate fuels in the United States are expected to increase over the next 20 years (Bond et al. 2014).

Interestingly, there has been a flurry of research activity since 2012 focusing on furfural as a biomass-derived platform chemical, more so than would be expected based on forecasted demand and prices.

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

The most obvious leveraging opportunity to accelerate scale-up is the emerging cellulosic ethanol industry and the existing corn ethanol industry. The most common feedstock for furfural production is corn cobs, which is available as a residue in corn ethanol facilities. In fact, POET-DSM Advanced Biofuels is using primarily corn cobs as feedstock for cellulosic ethanol production in their Emmetsburg, Iowa, facility (POET 2014a). Delft University of Technology presented a high-level strategy for integration with existing ethanol biorefineries, although the finer details are not provided (Marcotullio 2013).

In 2011, the Department of Energy provided $30 million in funding to Lignol Innovations, Inc., for a demonstration-scale biorefinery project to produce furfural, high-purity lignin, and cellulosic ethanol from hardwood (Suncor 2008, EERE 2011). The facility was scheduled to be located at Suncor Energy's Commerce City, Colorado, petroleum refinery. Suncor was scheduled to be the in-house customer for all ethanol produced by the facility (Lignol 2014). It is worth noting that Lignol Innovations decided to change the process configuration, feedstock, and product slate to make the project more commercially viable, which caused the effort to fall outside criteria originally established for DOE funding. As a result, Lignol Innovations is moving forward without DOE funding (Jessen 2011).

Furfural was listed as a top value-added chemical from biomass in a 2010 peer-reviewed publication that re-visited the Department of Energy's top 10 bio-based products from biorefinery carbohydrates (Bozell and Petersen 2010). The report indicates that furan-based chemicals, such as furfural, were omitted from the original list of promising bio-based products because of a static market and low yields, but technology development has improved the yields of sugar conversion to furans, increasing their potential as platform chemicals in biorefineries.

Glycerin

Glycerin (Figure 17) is a polyol (sugar alcohol). It is a main component of triglycerides found in animal fats and vegetable oil. The word ‘glycerin’ generally applies to commercial products containing mostly glycerol, whereas the word ‘glycerol’ most often refers specifically to the chemical compound 1,2,3-propanetriol and to the anhydrous content in a glycerin product or in a formulation (Ayoub and Abdullah 2012). In the literature addressing markets, “glycerin” is generally used instead of “glycerol” therefore “glycerin” will be used for the remainder of this section.

Glycerin is the main byproduct of biodiesel production. It is also generated in the oleochemical industry during soap production and is produced synthetically from propene. Biodiesel and soap production accounts for most current glycerin production; therefore the overall supply of glycerin is driven primarily by demand for these products. Glycerin from biomass is a drop-in replacement for synthetic glycerin (from propene). The most common use is as a humectant (hygroscopic substance) in food and personal care products, but glycerin has over 1,500 uses. The glycerin market is currently saturated, which has resulted in stable, low glycerin prices. As a result, the primary market driver for producing glycerin may be leveraging the stable, low prices by using glycerin as a feedstock for conversion to more valuable products, such as epichlorohydrin and succinic acid. The low, stable prices may also allow emerging uses, such as for animal feed and marine fuel, to become economically viable.

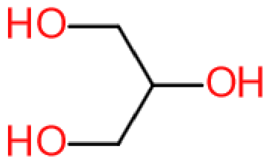

Figure 17. The chemical structure of glycerin ($C_3H_8O_3$)

Production from Petroleum

The most common petrochemical route to glycerin is from propene using the allyl chloride-epichlorohydrin (ECH) process (Figure 18). Propene is first chlorinated to allyl chloride. The allyl chloride is then oxidized with hypochlorite to dichlorohydrin, which is converted to epichlorohydrin by ring closure with calcium or sodium hydroxide. Hydrolysis of epichlorohydrin to glycerin is carried out using sodium hydroxide or sodium carbonate (Ullmann's 2003).

Synthetic glycerin accounts for about 12% of the glycerin market and is restricted to specialty applications that require high product standards. An example of an ECH synthetic glycerin process is Dow’s OPTIM synthetic glycerin product (The Dow Chemical Company 2014).

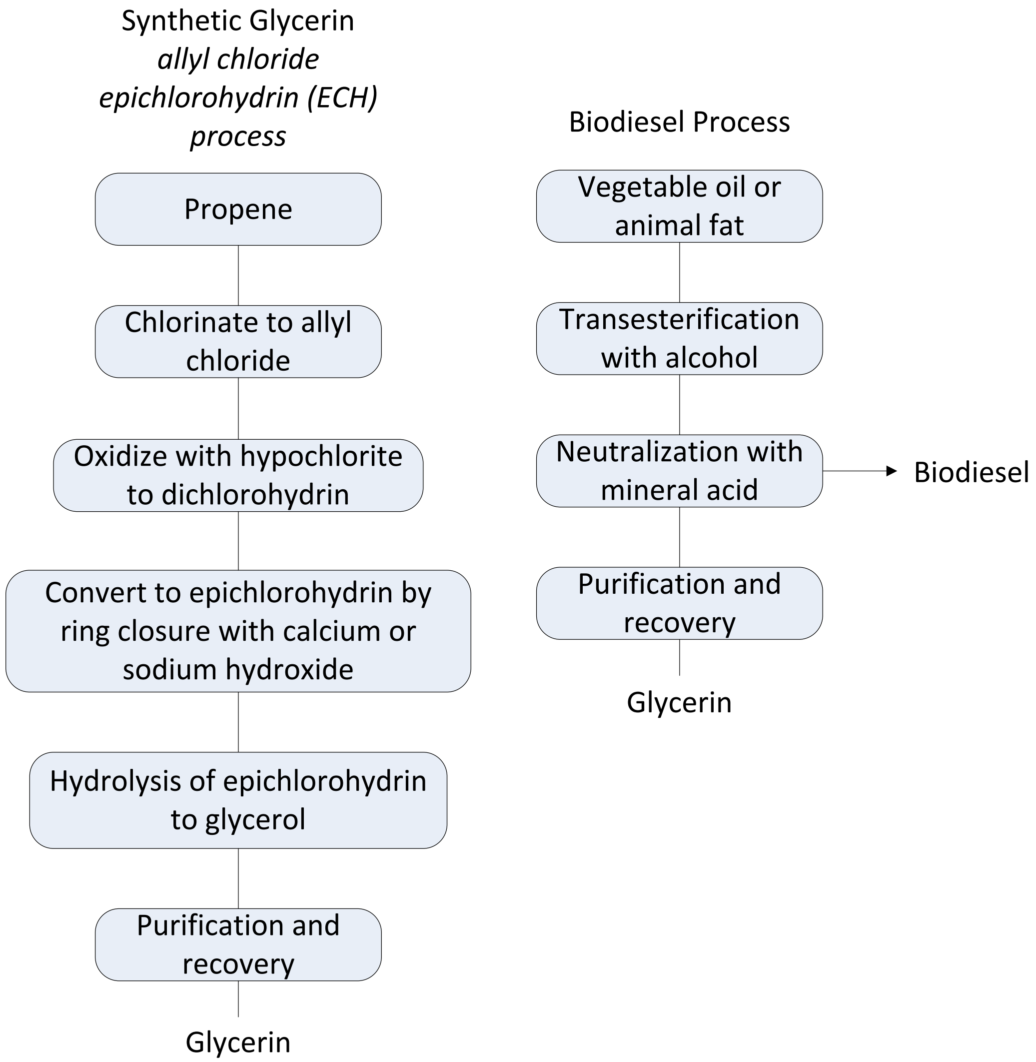

Figure 18. Synthetic and biodiesel production pathways for glycerin

Consumption and End Products

There is a small disagreement and inconsistency in the literature regarding quality specifications for different grades of glycerin, although most sources divide glycerin into two categories: crude and commercial. Refined glycerin, also referred to as commercial glycerin, is further divided into several grades based on industry standards (Ayoub and Abdullah 2012). When reviewing glycerin publications, care should be taken to ascertain the percent glycerin content of the glycerin product, as terms such as technical grade, commercial grade, crude, purified, and refined are used inconsistently across the literature.

Crude glycerin, a byproduct of the biodiesel industry, is the least concentrated form of glycerin, having a concentration ranging from 40%–88%, while purified or technical grade glycerin is usually considered 98%–99.8% pure and is used as a building block in the chemical industry, but not for food, pharmaceutical, or cosmetic manufacture. Refined or commercial grade glycerin is

96%–99.7% pure. The quality specifications for refined glycerin are generally set by U.S. Pharmacopeial Convention (USP) standards or Food Chemicals Codex (FCC) standards. In fact, glycerin is often referred to as "USP grade" or "FCC grade" (Quispe, Coronado, and Carvalho 2013). Technical grade glycerin is another refined specification, albeit slightly less concentrated than USP or FCC grade.

Industrial applications and end products of glycerin are listed in Table 6, along with the percent of the glycerin market consumed by each application.

Table 6. Glycerin Industrial Applications (Katryniok et al. 2010)

End Use/Application	% of glycerin produced
Drugs/Pharmaceuticals	18%
Personal Care/Cosmetics	16%
Polyether	14%
Food	11%
Triacetin	10%
Alkyd Resins	8%
Tobacco Products	6%
Explosives	2%
Cellophane	2%
Detergents	2%
Other	11%

Other literature sources report slightly different percentages for each application, but regardless, food, cosmetics, and pharmaceuticals consume the majority of the glycerin produced.

The growth of the biodiesel industry has saturated the crude glycerin market, therefore an active area of research is identifying new applications for the excess supply. Table 7 lists uses for glycerin in addition to those listed in Table 6. Some of the uses listed in Table 7 are already commercially proven but currently occupy a small share of glycerin consumption. Other uses are still under development.

There are 1,500 (Ayoub and Abdullah 2012) to 2,000 (Quispe, Coronado, and Carvalho 2013) industrial uses for glycerin. More comprehensive lists of glycerin applications can be found in the References section (Ayoub and Abdullah 2012, Johnson and Taconi 2007, Quispe, Coronado, and Carvalho 2013, Tan, Aziz, and Aroua 2013).

The glycerin market is currently saturated and prices are at historic lows, making other uses for low-value crude glycerin (with little or no purification) more economically plausible (Yang, Hanna, and Sun 2012):

- As a high-boiling point organic solvent to enhance enzymatic hydrolysis of lignocellulosic biomass during atmospheric autocatalytic organosolv pretreatment

- As an organic carbon source in wastewater denitrification
- As a fuel for generating electricity in microbial fuel cells
- As bio-oil by the co-liquefaction of co-hydrothermal pyrolysis with manure
- As burner fuel, if the price of glycerin is low enough (about $110/metric ton glycerin) (Ayoub and Abdullah 2012).

Table 7. Value-Added Opportunities for Glycerin

End Use/Application	Notes
Animal feed	This is a commercially proven and attractive option due to increasing corn prices and decreasing glycerin prices. Crude glycerin can be used (Ledbetter 2012, Yang, Hanna, and Sun 2012).
1,3-propanediol	Crude glycerin can be fermented to 1,3-propanediol (Tan, Aziz, and Aroua 2013, Yang, Hanna, and Sun 2012). A combined biodiesel 1,3-PDO process may reduce costs (Mu, Xiu, and Zhang 2008).
Citric acid	This is produced by fermentation of crude glycerin using *Yarrowia lipolytica* (Yang, Hanna, and Sun 2012).
Hydrogen	Crude glycerin can be converted to hydrogen using the bacterium *Rhodopseudomonas palustris* or through gasification (Yang, Hanna, and Sun 2012).
Polyhydroxy alkanoates (PHA) and polyhydroxy butyrate	These naturally occurring bacterial polyesters are recognized as good substitutes for non-biodegradable petrochemical polymers (Yang, Hanna, and Sun 2012).
Succinic acid	The bacterium *Basfia succiniciproducens* has been identified for succinic acid production (Yang, Hanna, and Sun 2012). Coproduction of succinic acid may increase the profitability of the biodiesel plant by 60% (Vlysidis et al. 2011).
Acrolein	Acrolein is used as an intermediate for the synthesis of acrylic acid, in the manufacture of paper, and as a microbiocide in oil wells.
Fuel	Glycerin can be co-digested in anaerobic digesters, or converted to various fuel additives in gasoline and diesel engines. The heating value of glycerin ranges from 16.1–19.6 MJ/kg, depending on the raw material used to produce it (Quispe, Coronado, and Carvalho 2013). Fuel for marine shipping is also an option (Bartlett 2013).
Epichlorohydrin	Epichlorohydrin is a high volume commodity chemical used in epoxy resins (Bell et al. 2008).
Propylene glycol	ADM has already commercialized hydrogenolysis of glycerin to propylene glycol (ADM 2015d).

Price History and Volatility

The price history for glycerin is difficult to report, as there are several grades and specification categories available, and the source of glycerin can affect the price as well. Most literature sources present price history on a refined or crude basis. Figure 19 and Figure 20 show the price history for different purities of glycerin. As can be seen by the price history graphs, the price of refined glycerin is fairly stable, except for a short-term spike in 2007 due to escalating prices of seed oils (Ayoub and Abdullah 2012). Glycerin prices are relatively stable primarily because the market is saturated. Crude glycerin is the starting material for refined glycerin, therefore an excess supply of crude glycerin keeps refined glycerin prices stable and at historic lows. The amount of glycerin refined to USP, FCC, or technical grade is dictated by demand for those specific grades. Current prices are around $1.10/kg ($1,100/metric ton) for the highest quality (FCC, USP grade) glycerin and $0.22–$0.66/kg ($180–$540/metric ton) for lower grades (Deshmane 2014).

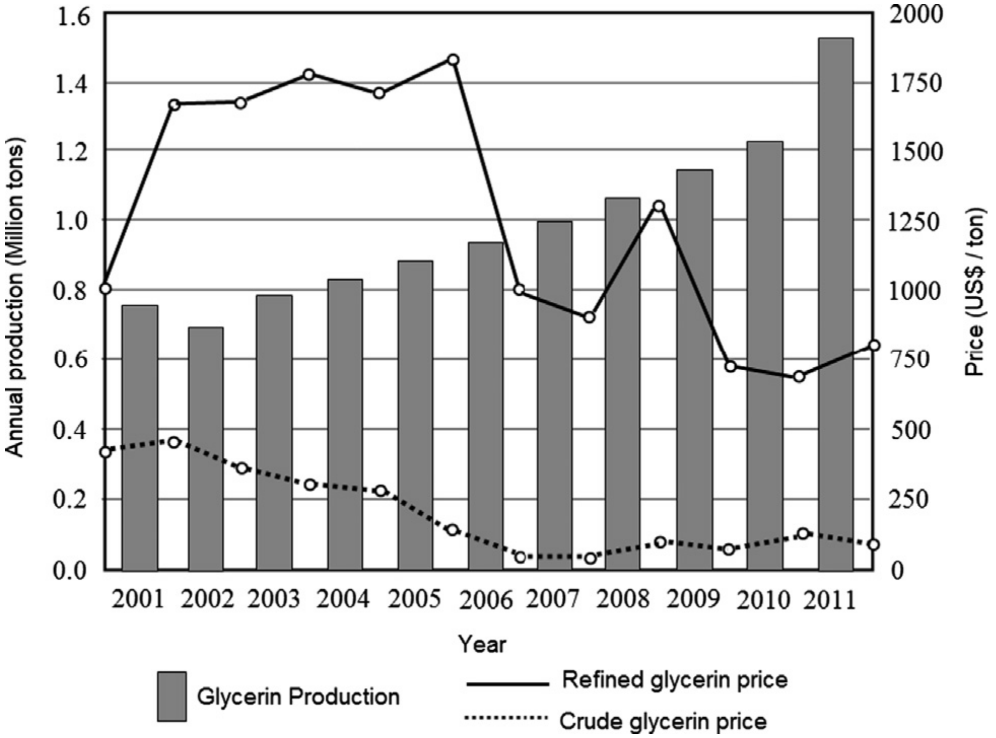

Figure 19. Global glycerin production and prices as of 2010; 2011 data is a projection (Quispe, Coronado, and Carvalho 2013)[5]

Current U.S. Market Status

The U.S. glycerin market is at a mature stage and is currently saturated, therefore prices can be expected to remain low provided biodiesel production holds steady or increases. If supply grows as a result of increased biodiesel production (unlikely in the United States), the emphasis should

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[5] Reprinted from *Renewable and Sustainable Energy Reviews*, 27, César A.G. Quispe, Christian J.R. Coronado,João A. Carvalho Jr., "Glycerol: Production, consumption, prices, characterization and new trends in combustion," 475-493. Copyright (2013), with permission from Elsevier.

be on widening the customer base and end-uses, especially for crude glycerin (Ayoub and Abdullah 2012). The current low prices of crude glycerin make it attractive for refining to higher grades, especially if it is used as a substitute for higher priced products.

Some companies are taking advantage of the low, stable price of crude glycerin. Enervation Advisors, LLC purchased a 5 MMgal/yr biodiesel and glycerin refining facility in Keokuk, Iowa, that sat idle for three years. Enervation says: “If you are fairly sharp, you are going to make money making glycerin because it’s a very stable environment.” It should be noted that Enervation’s business model is purchasing distressed assets, rather than building new facilities (Geiver 2011).

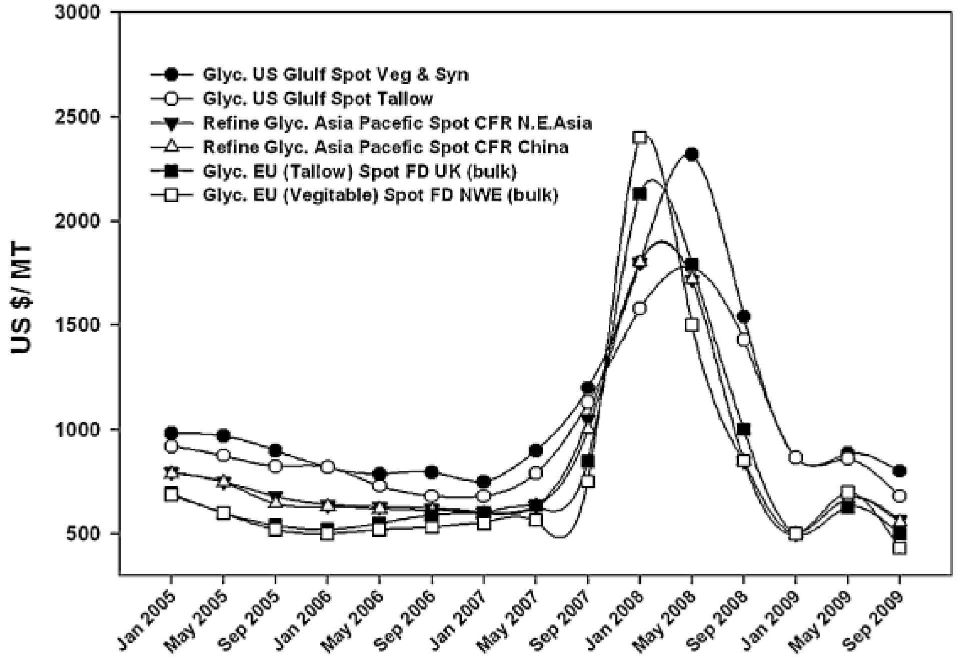

Figure 20. Price history for different types of refined glycerin (Ayoub and Abdullah 2012)[6]

Production from Renewable Sources

Natural glycerin is produced as a byproduct of soap production (saponification) or biodiesel production (transesterification) (Quispe, Coronado, and Carvalho 2013). Glycerin is the main byproduct of biodiesel production; about 1 pound of glycerin is generated for every 10 pounds of biodiesel (Quispe, Coronado, and Carvalho 2013). The most common form of glycerin sold by biodiesel producers is raw glycerin that results from biodiesel production from vegetable oil or fat (Choi 2008).

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[6] Reprinted from *Renewable and Sustainable Energy Reviews*, 16, Muhammad Ayoub, Ahmad Zuhairi Abdullah, "Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry," 2671-2686. Copyright (2012), with permission from Elsevier.

As glycerin is a byproduct of biodiesel production, there is not a current state of technology for glycerin production by itself, but rather a current state of technology for biodiesel production followed by glycerin refining. Biodiesel is typically produced via transesterification of triglycerides with an alcohol, usually methanol or ethanol, to produce biodiesel and glycerin. Stoichiometry requires 3 moles of alcohol for every 1 mole of triglyceride, but in practice 100% excess alcohol is used to force the transesterification reaction to a high yield. Two phases are formed, one rich in methanol and the other rich in biodiesel. Glycerin is present in both phases, although most is contained in the methanol phase. Biodiesel, methanol, and glycerin are separated in a series of evaporators and decanters, followed by final purification of the biodiesel in an absorber to remove soluble glycerin (Quispe, Coronado, and Carvalho 2013).

This low-grade crude glycerin contains 60% to 70% glycerin, with the balance being water, salt, and other organic materials such as methanol and free fatty acids (Thompson and He 2006). The most common method for refining glycerin is distillation. The advantages of distillation are that it is an established technology and it produces high-purity glycerin. However, distillation is an energy-intensive process due to the high heat capacity of glycerin. Ion-exchange is another purification option that has been used commercially, although the high salt content of glycerin from biodiesel production often makes ion exchange uneconomical (Lancrenon and Fedders 2008, Tan, Aziz, and Aroua 2013). Alternative purification strategies have been developed recently, most of which employ a combination of technologies such as acid protonation followed by physical filtration (Tan, Aziz, and Aroua 2013) and chromatographic separation followed by evaporation and ion-exchange (Lancrenon and Fedders 2008). The most cost-effective purification strategy may be specific to the composition of crude glycerin produced, as the nature of the crude glycerin is dependent on the feedstock used for biodiesel production and the catalyst used during transesterification (Tan, Aziz, and Aroua 2013).

No commercial efforts to produce glycerin from cellulosics could be found in the literature or trade publications, although triglycerides formed during algae growth may be suitable candidates from a technical standpoint. The high cost of algae production and low selling price of crude glycerin most likely makes algae an economically unviable feedstock for glycerin production. Another algae application is using glycerin as a heterotrophic carbon source, instead of sugar. According to research at Clemson University, 1 gram of glycerin yields about 0.5 grams of algae containing 50% to 60% lipids (Kotrba 2014).

Whole Energy completed construction of a glycerin processing facility in 2013 in Mt. Vernon, Washington. The facility has a capacity of 270 metric tons per week, but is currently operating at 36 metric tons per week, and is actively seeking customers. Whole Energy's glycerin is 92% to 98% glycerin and still has an odor and dark color. They intend to add polishing steps—potentially activated carbon—to remove contaminants that affect the color and odor (Deshmane 2014).

Data Gaps

The cost to produce natural glycerin of crude specifications is virtually negligible, as it is a byproduct stream of biodiesel production. The final cost of natural glycerin is determined by the desired purity, the refining method, and economies of scale. In fact, small biodiesel facilities often find landfilling crude glycerin more economical than refining. No recent data on the cost of refining crude glycerin was found, although a 2004 dollar estimate places the cost at $0.23–

$0.38/kg ($380/metric ton), depending on the size of the biodiesel facility (Kleber 2004). Distillation is needed to achieve a 99.7% pure glycerin to meet the required USP specifications, but distillation comes with high energy costs and often requires a separate building equipped with stainless steel piping (Geiver 2011).

Combustion in the marine shipping industry is an application with the potential to displace petroleum-derived fuel (Bartlett 2013). Performance tests on engines, and capacity assessments in marine applications, would be helpful in evaluating the technical and economic potential of using glycerine for marine applications.

Market Forces/Drivers: Why this Bioproduct?

Macroeconomic forces dictate the demand for refined glycerin (Landress 2014), and the diverse range of end-uses makes demand for refined glycerin relatively stable. U.S. biodiesel production is heavily influenced by the Federal Renewable Fuel Standard and tax credits. As a result of the renewal of tax credits, biodiesel production increased from 2011 through 2013, reaching 1.8 billion gallons of biomass-based diesel (primarily biodiesel, but it also includes renewable diesel) (National Biodiesel Board 2014). The biodiesel tax incentive has expired three times in the last 5 years, each time disrupting biodiesel production (Landress 2014).

Some companies view the saturated crude glycerin market as an opportunity. Renewable Energy Group, a biodiesel producer, says: “Until you have billions of gallons of biodiesel being made in the U.S. and Europe, there isn’t enough security in using glycerin for products typically made from petroleum” (Geiver 2011). The logic is that a stable, saturated glycerin market will create the certainty necessary for end-users to substitute glycerin for petroleum-derived products where possible. Renewable Energy Group continues: “Chemical companies will find a way to make products out of glycerin, that is the future” (Geiver 2011). A potential downside to this strategy is that creating new demand for glycerin, through innovation, may very well increase demand such that glycerin prices increases, potentially out of the range of new applications.

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

The most obvious opportunity to accelerate scale-up is increasing production capacity of the biodiesel industry. The biodiesel industry and infrastructure is already in place to produce large amounts of glycerin. A good example is the Enervation Advisors facility described above, which takes advantage of idle biodiesel infrastructure (Geiver 2011).

The Department of Energy’s fuel testing facilities and gasification pilot facilities can be used for glycerin combustion and gasification testing.

A “Hydrogen from Glycerol” feasibility study was conducted in 2009 (Ahmed, Papadias, and Farmer 2010). Results indicate hydrogen can be produced for $4.86/kg ($4,860/metric ton), based on a crude glycerin price of roughly $220/metric ton. A similar project was evaluated by Virent Energy Systems, but economic results were not reported (Virent 2007).

A project to develop fuel-flexible burners for the metal processing industry determined that a flow-blurring low-emission burner is capable of operating cleanly on natural gas as well as glycerin (Gemmer 2014).

DOE funded glycerin refining projects with Venoil LLC in 2010 (DOE 2010) and Whole Energy in 2012 (DOE 2010).

Isoprene

Isoprene is the building block for polyisoprene rubber, styrene co-polymers, and butyl rubber (Figure 21). Currently all commercially available isoprene is derived from petroleum. The majority of isoprene has typically been produced by separating the C5 stream from ethylene crackers fed with heavier feedstocks like naphtha or gas oil. Recently, steam crackers in the U.S. have shifted towards using lighter feedstocks like ethane, propane and butane which are byproducts of shale gas production. These lighter feedstocks have increased ethylene yields but have negatively impacted isoprene production. This has created a favorable opportunity for bio-based isoprene to enter the market. Bio-based isoprene, produced by aerobic bioconversion of carbohydrates, is identical to petroleum based isoprene and functions as a drop-in replacement molecule. Production of isoprene from biological sources is in the early stages of development but is accelerating with the backing from major tire manufactures (Bridgestone Corporation, Goodyear, and Michelin).

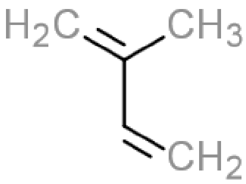

Figure 21. The chemical structure of isoprene (C_5H_8)

Production from Petroleum

Ethylene and propylene production drives the economics of steam crackers. Historically naphtha has been the feedstock of choice for steam crackers with the four- and five-carbon molecules, including isoprene, as valuable byproducts of that process. Shale gas production in the United States has increased the availability of inexpensive, lighter feedstocks like ethane, propane, and butane for ethylene production. Lighter feedstocks like ethane can dramatically increase the ethylene yield from a steam cracker. This may be a favorable result for steam cracker economics but ethane cracking produces no four- and five-carbon byproducts impacting the supply of isoprene (Gentry 2013).

Figure 22 presents a high-level overview of isoprene production from both biomass and traditional petroleum sources. Isoprene produced via cracking naphtha or gas oils to ethylene is recovered from the butane/butene stream. This was a primary source of isoprene in the United States but virtually no isoprene is produced from ethylene crackers that have shifted to using ethane, propane, and butane as feedstock (Gentry 2013). A concentrate of the isoprene byproduct is further processed using extractive distillation to produce a high-purity product. Russian companies use a less common synthetic route to produce isoprene from petroleum using isobutylene and isopentane.

Russia is the world's top producer of isoprene with Nizhnekamskneftekhim being the world's largest producer followed by Goodyear (Bourzac 2010, Alperowicz 2013, IHS 2015a). During the 1970s and 80s the former Union of Soviet Socialist Republics (USSR) made a commitment to become independent of natural rubber and invested heavily in isoprene production. Production decreased after the breakup of the USSR. Some capacity has been idled, closed, or shifted to other products like methyl tertiary butyl ether (MTBE) and butadiene.

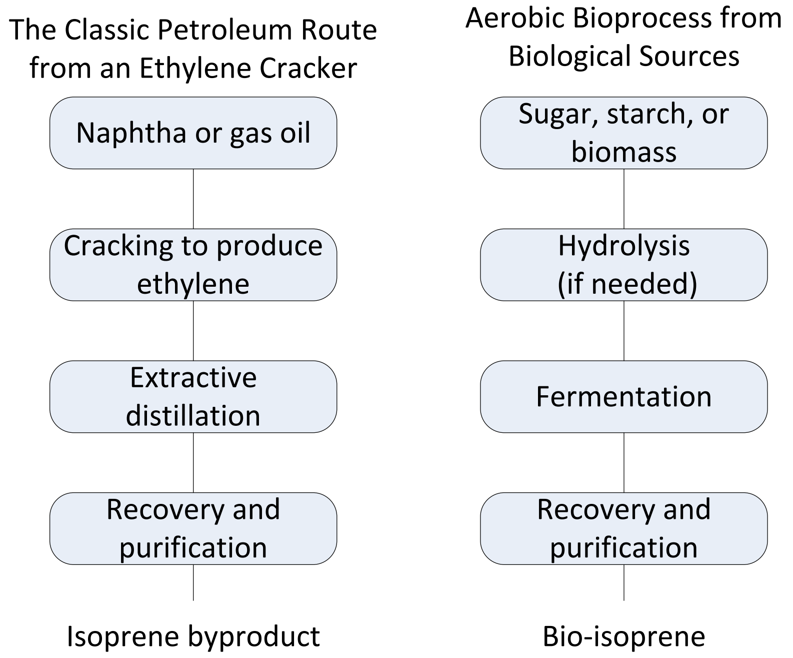

Figure 22. An overview of isoprene production pathways from petroleum and renewable feedstocks

Consumption and End Products

Total world consumption of isoprene in 2008 was 800,000 metric tons (GlycosBio 2010). About 60% of it was used to produce polyisoprene rubber, styrene co-polymers, and butyl rubber used for manufacturing tires. About 30% was used to produce adhesives and the balance was used for medical or personal care applications. Tires are the dominant market for isoprene and demand for isoprene-based products typically follows the health of the transportation sector. In 2013, Russia and the United States account for roughly two-thirds of the total world consumption of isoprene (IHS 2014e).

Price History

There is a great deal of confidentiality in pricing isoprene. Special and long-term pricing arrangements are common in this market. Publicly available prices from 2010 reflect trends rather than hard data and those trends suggest $1.60–2.30/kg (GlycosBio 2010).

Current U.S. Market Status

Growth in isoprene consumption has slowed since the 1990s. Goodyear, Shell, Exxon, Dow, and LyondellBasell are the leading producers of isoprene in the United States. Styrene-isoprene-styrene (SIS) copolymers accounted for 41% of U.S. isoprene consumption in 2010. Kraton Polymers in Belpre, Ohio, is the global market leader for SIS and other styrenic block copolymers, producing 200,000 metric tons per year. Dexco Polymers in Plaquemine, Louisiana, is the other major U.S. producer at 35,000 metric tons per year. U.S. SIS production has slowed as isoprene costs have increased. Some consumers have substituted SIS for styrene-butadiene polymers or acrylics as costs have risen. Polyisoprene (PI) accounted for 32% of U.S. isoprene consumption. Goodyear and Kraton are the largest U.S. producers of PI at 90,000 and 25,000 metric tons, respectively. Tires account for 60% of the PI consumption. Butyl rubber accounted for 6% of U.S. isoprene consumption. ExxonMobil plants in Texas and Louisiana are the dominant U.S. producers of butyl rubber.

Production Pathways from Renewable Sources

Carbohydrate-rich streams can be converted to isoprene through an aerobic biological conversion process. Following conversion, the bio-isoprene can be recovered in the gas phase, simplifying purification to meet product specifications (GlycosBio 2010). A further benefit of having the product in the gas phase is that it can minimize feedback inhibition on further product synthesis (Lane 2014d, Whited et al. 2010).

Amyris has partnered with Michelin to produce bio-isoprene from glucose using genetically modified *Saccharomyces cerevisiae* yeast. Their effort has 2015 as an end date. Successful research on their part is expected to lead to a more mature partnership or joint venture.

Goodyear and DuPont (Genencor) have jointly invested in R&D and secured intellectual property for an engineered *E. coli* that produces bio-isoprene from biomass feedstock. Wild-type *E. coli* can naturally produce some isoprene. The engineered strain produces increased isoprene synthase and its metabolism has been modified to overproduce 3,3-dimethylallyl pyrophosphate, an isoprene precursor (Bourzac 2010). Reported volumetric productivity was 2 g/L/h with a 30% yield of isoprene from glucose. Goodyear and DuPont are expected to invest in pilot facilities in 2015–2016 (Lane 2014d).

Data Gaps/Potential R&D Needs

There is a lack of public data available for the costs of bio-isoprene capital, operating, and product costs. Like other bioproducts, bio-isoprene production would require clean, inexpensive sugars from lignocellulosic biomass to compete with commodity sugar and starch substrates. Bio-isoprene is produced by aerobic bioconversion. Compared to anaerobic fermentation, aerobic bioprocesses demand higher capital and operating costs for costly reaction vessels and compressors.

Market Forces/Drivers: Why this Bioproduct?

There are two drivers pulling bio-isoprene to the market. First, the shift to lighter feedstocks for ethylene cracking has decreased the supply of petroleum based isoprene. This has opened an opportunity for isoprene from non-traditional sources to gain traction in the market. Second, there is strong corporate interest in producing products from renewably sourced isoprene. Goodyear and Michelin are market champions for bio-isoprene. They have strong interest in producing tires made with renewable materials. “Finding a replacement for oil-derived materials is the right thing to do from a business standpoint, but it’s also the right thing to do for the environment,” says Jean-Claude Kihn, chief technical officer for Goodyear. “Since synthetic rubber is a critical component to our products and many others, we are very excited to be working on this renewable alternative with DuPont” (Goodyear 2012).

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

Isoprene oligomers have attracted attention as fuel precursors. There are nearly 1,200 citations for isoprene on the www.osti.gov site, suggesting strong interest. Like other aerobic pathways, isoprene production from biomass will benefit from pretreatment technologies that produce clean, inexpensive sugars from lignocellulosic feedstocks.

Lactic Acid

Lactic acid ($C_3H_6O_3$) is the most widely occurring carboxylic acid in nature (Figure 23). Most commercial production of lactic acid is by microbial fermentation of carbohydrates. It was first isolated in 1780 by a Swedish chemist, and the first commercial production started in 1881 in Littleton, Massachusetts (Ren 2010). It is an alpha-hydroxy acid with dual functional groups making it suitable for use in a variety of chemical transformations and products. Lactic acid is used globally for applications in food, pharmaceuticals, personal care products, industrial uses, and polymers. It has two isomeric forms, L-(+)-lactic acid and D-(-)-lactic acid. L-(+)-lactic acid (Figure 23 A) is the most common form and is naturally produced from pyruvate in the normal metabolism of microorganisms, animals, and humans. D-(-)-lactic acid (Figure 23 B) is formed in a racemic mixture of isomers from chemical synthesis. It may also be produced by fermentation, again as a mixture of isomers from certain microorganisms, or it may be produced as an optically pure product from engineered microbes. The D-isomer is often blended with the L-isomer to create polylactic acid (PLA) copolymers with properties like thermal stability that exceed those of a pure, single isomer PLA product. PLA is a renewable and biodegradable polymer and is expected to be the biggest driver for growth in lactic acid demand.

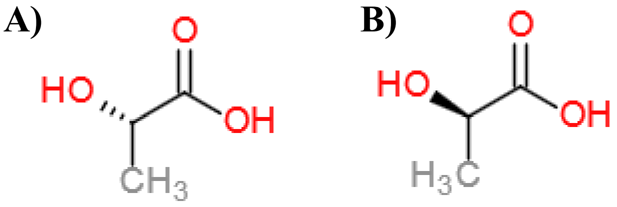

Figure 23. L-(+)-lactic acid (A) and D-(-)-lactic acid (B)

Production from Petroleum

Most lactic acid is produced by microbial fermentation of carbohydrates. However, a relatively small amount is produced by chemical synthesis, using acetaldehyde as a starting material. Figure 24 shows a high level overview of the two approaches. Microbial routes to lactic acid are discussed in the *Production from Renewable Sources* section below.

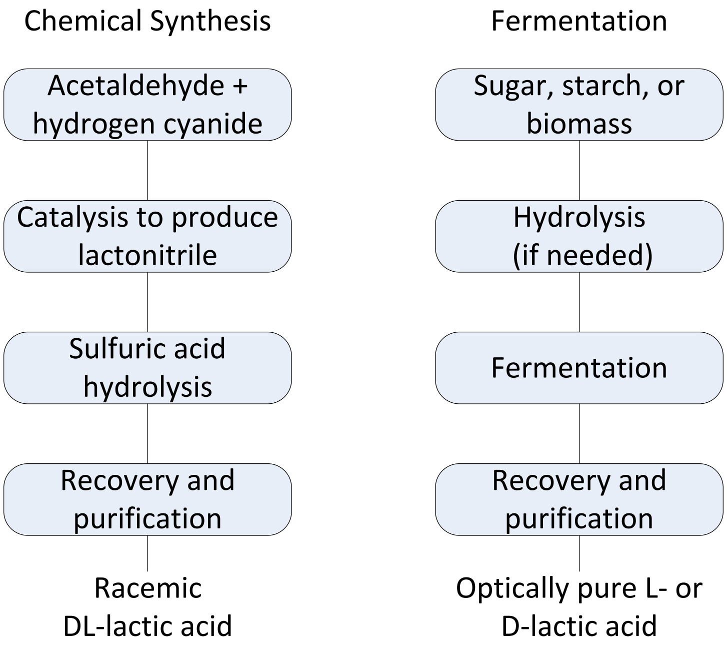

Figure 24. An overview of lactic acid production pathways from petroleum and renewable feedstocks

Musashino Chemical Laboratory, Ltd., in Tokyo, Japan, is the sole producer of synthetic lactic acid, producing on the order of approximately 7,000 metric tons per year, or about 2% of global lactic acid production (Musashino Chemical Laboratory). Chemical synthesis uses acetaldehyde and hydrogen cyanide to produce lactonitrile. Hydrogen cyanide is primarily produced from natural gas or as a byproduct of acrylonitrile production. Acetaldehyde is produced by oxidation of ethylene, hydration of acetylene, or from oxidation or dehydrogenation of ethanol. Lactonitrile from the synthesis is recovered by distillation and hydrolyzed to lactic acid using mineral acids with an ammonium salt as a byproduct. The lactic acid product is a racemic mixture of D- and L-isomers (Ren 2010).

Consumption and End Products

Lactic acid is used as an acidulant, flavoring agent, pH buffer, and spoilage inhibitor in food applications. It is listed as Generally Recognized as Safe (GRAS) by the U.S. Food and Drug Administration (FDA). It is non-volatile and odorless. Esters of lactic acid are used as emulsifiers for baked goods. Other applications include use in tanning and textile finishing operations. L-lactic acid is biocompatible and is therefore used in food, pharmaceuticals, and personal care products. D-lactic acid is used along with L-lactic acid to produce PLA. PLA production is expected to be the main driver for growth in lactic acid consumption.

There are three processes used to make high molecular weight PLA polymers from D-(-)-lactic acid and L-(+)-lactic acid (Ren 2010):

1. Direct polycondensation is used to produce low molecular weight polymers (1,000–5,000 Da [dalton, or unified atomic mass unit]). Chain coupling agents can be used to link these to form high molecular weight polymers (>100,000 Da).
2. Polymerization through lactide formation begins with a low molecular weight pre-polymer (as above). These units are linked using a ring-opening lactide polymerization to form high molecular weight polymers.
3. The above methods are limited by their ability to remove the water byproduct produced during polymerization. Azeotropic dehydration polycondensation overcomes those limitations by using high boiling point solvents that remove water azeotropically by distillation during the polymerization reaction.

PLA has a polyester structure. Homopolymers that use only a single isomer suffer from properties like brittleness and low thermal stability. Co-polymers that incorporate a blend of each isomer have higher melting points, higher glass transition temperatures, and improved mechanical properties versus pure L- or D-homopolymers (Ren 2010). PLA formulations can also be modified with plasticizers or coupling reagents depending on the intended application (Wool and Sun 2005). PLA has properties that make it attractive for use in disposable or biodegradable applications such as utensils, food packaging, trash bags, and other consumer products. PLA is also used in high-value medical applications like sutures and tissue scaffolds due to its biocompatibility and biodegradability.

PLA is sold in number of grades depending on application. There are grades for extrusion and thermoforming, injection molding, films and sheets, fibers, injection stretch blown molded bottles, expanded foam sheet, and binders and adhesives (NatureWorks 2014b).

Price History and Volatility

Lactic acid is most often sold as an 88% solution for use as a starting material in all applications. The price varies depending on the market (e.g., food, pharmaceuticals, and PLA) and a range of \$1.30–\$2.30/kg has been reported (ICIS 2008, Higson 2011). In general, the price for lactic acid will follow the price of commodity starch and sugar feedstocks.

Current U.S. Market Status

Global lactic acid production was estimated to be 300,000–400,000 tons in 2013 (Harmsen, Hackmann, and Bos 2014, de Guzman 2012d). The U.S. is the largest producer, led by companies NatureWorks and Purac. Demand for lactic acid is expected to be strong in the near- to midterm, driven by demand for PLA (Harmsen, Hackmann, and Bos 2014). Marc Verbruggen, president and CEO of NatureWorks, recently spoke about the cumulative sales of their PLA product over the last decade: “in the world of bioplastics, having produced and sold a billion pounds means that we have come a long way” (Miel 2014). NatureWorks has seen average annual sales growth of 20%. Verbruggen also suggests that, “we’re going to get pretty quickly to a situation where growth is no longer depending on demand; it’s going to start depending on supply” (Miel 2014). Forecasts have estimated that global PLA capacity will exceed 800,000 tons by 2020 (Carus 2012). New global production will be needed to support growth and it is expected to shift to developing countries with lower wages and lower sugar costs. Purac recently commissioned a 100,000-ton-per-year plant in Thailand (EABC 2015).

Production from Renewable Sources

A partial list of current lactic acid producers and near-term planned expansions is given in Table 8. There was limited information available on plants in China. Most of the world's lactic acid is produced by anaerobic bacterial fermentation. Fermentation substrates are based on local availability and include corn starch, sugar beets, sugarcane, or wheat. Cellulac, Purac and NatureWorks are researching ways to use lignocellulosic biomass as a carbohydrate source to produce lactic acid.

Table 8. Current and Planned Lactic Acid Production Capacity (McCoy 2013, de Guzman 2012d).
(This list is not exhaustive as there is limited information on some of the plants located in China.)

Company	**Annual Capacity (metric tons)**	**Plant Location**	**Operational Date**
NatureWorks	150,000	Blair, Nebraska	2002
NatureWorks	150,000	Thailand or Malaysia	n.a.
Purac	50,000	Blair, Nebraska	1999
Purac	100,000	Thailand	2012
Purac	35,000	Brazil	n.a.
Purac	55,000	Spain	2008
ADM	30,000	Decatur, Illinois	1993
Cellulac	100,000	Ireland	2016
Galactic	15,000	Milwaukee, Wisconsin	2011
Galactic	50,000	Bengbu, China	2002
Futerro	1,500 (pilot scale)	Escanaffles, Belgium	2010
ThyssenKrupp Industrial Solutions	3,000	Guben, Germany	n.a.
Synbra Technology	1,000 (pilot scale)	Switzerland	2012
Synbra Technology	5,000	Etten-Leur, Netherlands	n.a.
Musashino Chemical Laboratory, Ltd.	7,000	Japan	n.a.
Henan Jindan Lactic Acid Technology Co., Ltd.	200,000	Henan Province, China	2011
Zhejiang Hisun Chemical	5,000	Zhejiang Province, China	1998
Nantong Jiuding Biological Engineering Co., Ltd.	3,000	Jiangsu Province, China	n.a.
Shenzhen BrightChina Industrial Co., Ltd.	10,000	Shenzhen, China	2002
Tong-Jie-Liang Biomaterials Co. Ltd.	1,000	China	2005

Chemical synthesis and some fermentations generate a racemic mixture of both D- and L-isomers. However, optically pure D-(-)-lactic acid can be produced by metabolically engineered microbes (Zhou et al. 2003, Cooper et al. 1988, Walsh and Venus 2013). Lactic acid bacteria can be divided into three groups based on their metabolic products. The homofermentative microbes produce 2 mols of L-(+)- lactic acid for each mol of glucose consumed. The main fermentation microbes in use today (*Lactobacillus*, *Streptococcus,* and *Pediococcus)* are in this category (Todar 2012). The heterofermentative microbes produce 1 mole each of L-(+)-lactic acid, CO_2, and ethanol for each mol of glucose consumed. The third group, also heterofermentative, produces a racemic mixture of D and L lactic acid with acetic acid and CO_2 as coproducts.

Traditionally, several steps are needed after fermentation to produce the final lactic acid product. Fermentation broths are neutralized with calcium hydroxide, which forms calcium lactate salt. The salt solution is filtered to remove microbial cells and evaporated to concentrate the solution. Sulfuric acid is added to hydrolyze calcium lactate and the insoluble gypsum is removed. Methanol is added to esterify the lactic acid and the final product is purified by distillation and a hydrolysis step.

There are other new technologies in use commercially to separate and purify lactic acid from fermentation broths. Technologies like electrodialysis or liquid-liquid extraction with an organic solvent can avoid some of the drawbacks of the traditional purification steps, such as gypsum formation and disposal (Ren 2010).

In Europe, Cellulac has produced lactic acid at the pilot scale from agriculture, brewery, and dairy waste. They are working to scale up their technology to 20,000 tons per year in Phase 1 and to 100,000 tons per year in Phase 2 of their plan (Cellulac 2013).

Verbruggen, of NatureWorks, gave some insight to the state of technology costs for lactic acid: “The variable sources of raw materials also will help the company remain cost competitive with traditional materials. Sugar currently sells on the global market for 17 to 20 cents per pound,” he says. “From a feedstock point of view, that sugar price means that PLA can compete against an oil-based feedstock selling at $50 per barrel, and oil currently is selling for far more than that” (Miel 2014).

Data Gaps

Scale-up of lactic acid production would require clean, cheap sugars from lignocellulosic biomass to compete with commodity sugar and starch substrates. There is a lack of data about lactic acid production and purification from biomass hydrolysates, including issues of C5 sugar utilization, although it appears work has started to address some of these issues. Gerard Brandon, CEO of Cellulac says: “With the support of the European Union we will convert, part of what was until recently, the 2nd largest brewery in Ireland into what will be the largest producer of lactic acid from agricultural waste and dairy byproducts” (Cellulac 2013).

ACRYLIC ACID

Acrylic acid has a large market share of about 5 million metric tons per year with projected growth rates of 4%–5% per year (Tullo 2014a, Bomgardner 2015c, de Guzman 2012a, Novomer 2013, Tullo 2013d, Nexant 2013). Acrylic acid is produced by the catalytic oxidation of propylene with air to form acrolein and then acrylic acid. With the availability of cheap shale gas utilized to produce ethylene, the market has seen a reduction in propylene production and is projecting higher costs for acrylic acid, opening opportunities for biomass-derived products (IHS 2014a).

Lactic acid is also being pursued as a precursor to the production of bio-derived acrylic acid by companies like Myriant and SGA Polymers (a spin-off of MATRIC). Alternative routes to acrylic acid are through 3-hydroxypropionic acid (3-HPA), a fermentation intermediate, followed by catalytic dehydration to make acrylic acid (Tullo 2014a). Cargill recently acquired OPX Biotechnologies, as well as the company's engineered microbes to produce 3-HPA, and is partnering with Novozymes to develop this pathway (Bomgardner 2015c). Myriant President and Chief Operating Officer Cenan Ozmeral notes that it is "much cheaper to make lactic acid at very high yields and at very high concentrations than 3-HPA" (Tullo 2014a). However, 3-HPA is much easier to upgrade as the terminal hydroxyl group in 3-HPA is easier to dehydrate than lactic acid, and Myriant has been working with researchers at MIT and Penn State to overcome these challenges (Tullo 2014a).

Acrylic acid production via sugars has also been patented by Genomatica through a fumaric acid intermediate (de Guzman 2012a). The French company Arkema scaled the production of acrylic acid to the pilot scale in 2010 utilizing a glycerin feedstock. The project was planned to be scaled-up further but was put on hold as it cannot currently compete with petroleum-derived acrylic acid due primarily to the cost of the glycerin feedstock (Tullo 2014a). Novomer is using waste streams rich in CO and utilizing chemical catalytic approaches to upgrade ethylene oxide to acrylic acid. This technology has received funding from the Office of Energy Efficiency & Renewable Energy's Clean Energy Manufacturing Initiative program in 2013 and the company has partnered with Saudi Aramco Energy Ventures to further scale up and commercialize the process (Novomer 2013, Tullo 2013d).

Market Forces/Drivers: Why this Bioproduct?

Major retailers like Target and Walmart, as well as consumer product companies like Procter & Gamble have suggested that PLA could be a way to meet their corporate sustainability goals (Miel 2014). Therefore, demand for PLA has pulled more lactic acid to the market. PLA is renewable, biodegradable, and has properties that make it a substitute for some petroleum-based plastics (Ren 2010). PLA is relatively low cost and available in a variety of grades to suit many applications (Harmsen, Hackmann, and Bos 2014). PLA is used to produce compostable service ware, grocery and waste bags, mulch films, and food packaging. It has found novel uses in medical applications like sutures, drug delivery, and as a tissue engineering scaffold.

A number of consumer product companies like Newman's Own, Whole Foods, and Walmart are pushing for increased use of PLA for packaging applications (Royte 2006). Yogurt maker Stonyfield Farm switched from petroleum-based polystyrene to PLA for its packaging in 2010 (Stonyfield Farm 2013). A life-cycle assessment from Stonyfield estimated 22% less total energy and 8% less greenhouse gas (GHG) emissions by switching to PLA packaging (de Guzman 2010b).

Most of the world's lactic acid is produced by anaerobic bacterial fermentation. Fermentation substrates are based on local availability and include corn starch, sugar beets, sugarcane, or wheat. All of the current feedstocks directly compete with food while cellulosic feedstocks would be outside of this area of competition. Several companies are working on lactic acid production from lignocellulosic biomass:

- Myriant produces L- and D-isomers of lactic acid from cellulosic material for use as a PLA feedstock. The company's D-(-)-lactic acid started production at commercial scale in June 2008. Myriant was awarded $50 million from DOE to support a production facility in Lake Providence, Louisiana (Myriant 2011).
- Direvo Industrial Biotechnology GmbH has developed microbes to convert lignocellulose to lactic acid. Direvo´s CEO Jorg Riesmeier states: "Our proprietary bacteria ferment grass, straw, and other agricultural and forestry wastes. We have improved yield and conversion rate dramatically over the last 18 months. Again, Direvo has proven the ability to rapidly develop novel biotech processes" (Direvo 2013).
- Cellulac is commissioning a 100,000-ton-per-year lactic acid production facility in Dundalk, Ireland. They have developed a "combined chemical and process engineering technology to produce lactic acid and associated industrial-scale biochemicals from second generation feedstocks, including lignocellulosic materials (such as wheat straw, distilled dried grains with solubles, and spent brewers' grains) and lactose whey" (Cellulac 2013).
- NatureWorks is "committed to a long-term plan to transition the current raw material supply to residual biomass. This is a key part of the Ingeo (NatureWorks brand PLA) journey to responsible innovation" (NatureWorks 2015).

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

There are nearly 4,000 citations for lactic acid on the www.osti.gov site, suggesting strong interest. Lactic acid is primarily produced by fermentation, making it compatible with other biochemical approaches to biomass conversion. Like other fermentation pathways, lactic acid production from biomass will benefit from pretreatment technologies that produce clean, inexpensive sugars from lignocellulosic feedstocks.

Propanediol (1,3-)

1,3-Propanediol is a linear aliphatic diol which makes it a useful chemical building block (Figure 25). It has attracted attention because of the wide variety of applications where it can be used including polymers, personal care products, solvents, and lubricants (Vilela et al. 2014, Zeng and Sabra 2011). A major driver for PDO production is as a component in polytrimethylene terephthalate (PTT) polymers. PTT has found use in textiles and fibers due to its superior durability and stain resistance compared to nylon (Corma, Iborra, and Velty 2007). PTT contains about one-third PDO and two-thirds terephthalic acid by weight. PDO has been produced synthetically from acrolein or ethylene oxide, but today bio-based PDO is the primary source of production. DuPont Tate & Lyle Bio Products Company is the largest producer of bio-based PDO. Bio-based PDO uses 40% less energy than the typical petroleum-based route giving the bio-based route a significant advantage. Terephthalic acid is made from petroleum and PTT containing bio-based PDO has been marketed as a green alternative to polymers like nylon and polyethylene terephthalate.

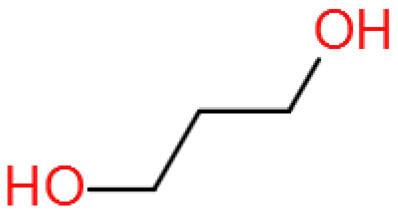

Figure 25. The chemical structure of 1,3-propanediol

Production from Petroleum

PDO is a relatively recent entrant to the petrochemical market and Shell Chemical Company was the primary producer of synthetic PDO from petroleum. In the 1960s Shell had investigated the production of PDO by hydration of acrolein. Producing PDO at the right cost and quality proved to be difficult and the commercial production of PDO was not realized until 1998 (Alan 1999). Shell's new process at that time (Figure 26) used a cobalt containing catalyst for the hydroformylation of ethylene oxide and syngas to 1,3-hydroxypropanol (HPA). The HPA was purified and subsequently hydrogenated to PDO (Powell et al. 1998). The PDO was then purified by distillation to create a fiber-grade feedstock to be used to produce PTT under Shell's trade name Corterra. Shell's production of synthetic PDO reached a peak of 83,000 annual tons at a manufacturing facility in Geismar, Louisiana (Kraus 2008). Bio-based production of PDO began in 2006 using glucose as a fermentation substrate. Petrochemical and biochemical PDO coexisted on the market for a few years. Then Shell closed its PTT plant in 2009, the main consumer of their PDO output, because it was never profitable (Reisch and Tullo 2009, CNW 2009). Now the majority of PDO is made using a bio-based process

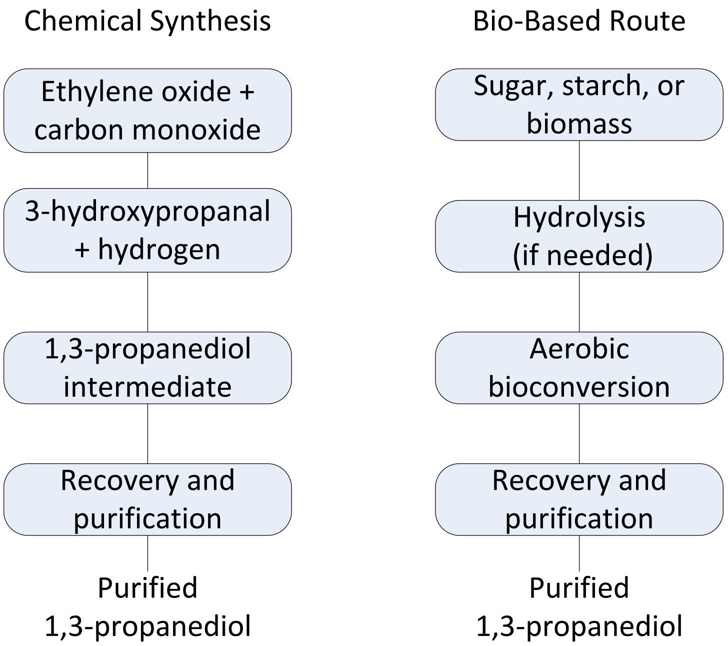

Figure 26. An overview of petrochemical and biochemical routes for producing PDO

Consumption and End Products

The diol structure of PDO makes it particularly useful for producing polyester materials like PTT, which is the major end product for most PDO production (Research and Markets 2015). DuPont had patented a formula for PTT in the 1940s (Rex and Tennant 1949). The desirable stain resistance and durability made it interesting to pursue but the historically high cost of making PDO had kept the polymer off the market.

Today, DuPont Tate & Lyle Bio Products Company is the largest producer of bio-based PDO. They market PDO under two trade names—Susterra for industrial and fiber applications and Zemea for personal care, cleaning, and food processing applications (DuPont Tate and Lyle BioProducts). Susterra is the feedstock for DuPont's PTT fibers under the trade name Sorona. Sorona claims to have one-third renewable material content based on the amount of bio-based PDO in their formulations. The other industrial applications for PDO include de-icing fluids, engine coolant, heat transfer fluids, polyurethanes, and unsaturated polyester resins.

Personal care applications include functional uses as a humectant, preservative booster, solvent, carrier, and viscosity modifier. It meets USP quality standards. In cleaning applications it is intended to act as a solvent and enzyme stabilizer. PDO has received the FDA's GRAS designation (Cheeseman 2010) and the USDA's 100% Biobased designation. It has also been approved as Kosher and Halal. Food applications include use as a humectant, preservative booster, and stabilizer.

Price History

PDO production is in the hands of only a few companies and pricing information is closely held. One source from 2005 suggested the market price was $2.20/kg (Crank et al. 2005). A second source suggested that in 2008 the market price was $1.76/kg (Kraus 2008). The change in price most likely reflects a number of factors including increased competitiveness as bio-based PDO went online in 2006.

Current U.S. Market Status

Estimated global demand for PDO in 2014 was 125,000 metric tons per year (Harmsen, Hackmann, and Bos 2014). The DuPont Tate & Lyle Bio Products plant in Loudon, Tennessee, has a capacity of 63,500 metric tons per year (Dupont tate and Lyle BioProducts 2015). The difference is presumably from suppliers in China; however, data about Asian plant capacities is unavailable in public sources. As mentioned above, most of the PDO is used in the production of PTT, which is Sorona in the U.S. market. DuPont has stated that they are expecting 4%–7% compound annual growth rate (CAGR) through 2017 for sales in the fiber category (Nielson 2014). This suggests a similar growth rate could be expected for PDO production.

Production Pathways from Renewable Sources

Biological production of PDO was first identified in 1881 by August Freund where glycerol was the substrate in a culture of *Clostridium pasteurianum* (Freund 1881). PDO production from glycerol fermentation was ultimately found widely in microorganisms including species from *Citrobacter*, *Clostridium*, *Enterobacter*, *Klebsiella* and *Lactobacillus genera* (Nakamura and Whited 2003). DuPont Tate & Lyle Bio Products currently produces PDO by aerobic bioconversion of glucose from wet milled corn starch (Nakamura and Whited 2003). DuPont Tate & Lyle chose to pursue production from glucose as refined glycerol prices were increasing in the early 2000s to more than $1,500 per metric ton (see Figure 19) (Nakamura and Whited 2003). In contrast, glucose prices from corn starch averaged $320 per metric ton from 1997 to 2006 (McConnell 2015). DuPont had partnered with Genencor to develop a genetically engineered *E. coli* that metabolized glucose to an intracellular glycerol intermediate that is then converted to PDO. Genetically engineering PDO production from glucose was complex because microbial metabolism demands additional co-factors (nicotinamide adenine dinucleotide and inorganic phosphate) for that pathway when compared to glycerol metabolism (Nakamura and Whited 2003). However, glucose was a rational substrate for their enterprise because of feedstock costs and Tate & Lyle's assets in the corn milling industry.

Glycerol prices dropped dramatically in 2006 as DuPont's bio-based process came online. This has renewed interest in using crude glycerol from biodiesel production as a feedstock for PDO production (Zeng and Sabra 2011). Crude glycerol is less pure and less concentrated than refined glycerol and typically has sold for below $200 per ton (Figure 19). The success of the DuPont Tate & Lyle process also suggests that glucose from cellulose is a potential substrate for PDO production.

METabolic EXplorer SA produces bio-based PDO in Clermont-Ferrand, France, but only at the pilot scale. Operations began there in 2009 (Pöyry Management Consulting 2010). They are planning a larger scale production facility with an 8,000-metric-ton-per-year capacity with the possibility to expand to 50,000 metric tons per year (Harmsen, Hackmann, and Bos 2014).

METabolic EXplorer has partnered with SK Chemicals in Seongnam, South Korea, to commercialize their technology (2014c). There are two companies in China pursing PDO production: Zhangjiagang Glory Biomaterial Co., Ltd., and Zouping Mingxing Chemical Co., Ltd. Data is unavailable on their capacities and production routes, which may be chemical or biological.

Data Gaps/Potential R&D Needs

The effective use of lignocellulosic feedstocks to produce bio-based PDO at a large scale will require additional research and process development to generate a clean stream of glucose to be compatible with today's genetically engineered PDO-producing microbes. Further work will be needed to develop microbes that can produce PDO from five-carbon sugars or crude, less purified biomass hydrolysate streams. Similarly, strain development will be needed to generate strains that can tolerate using the highly variable, low purity crude glycerol as a feedstock. Some progress has been reported in that area but more work is needed to have a strain that is relevant at industrial scale (Zeng and Sabra 2011). For example, anaerobic glycerol fermentation typically produces byproducts like acetic acid, formic acid, lactic acid, butyric acid, or ethanol, which reduce PDO yield and can be toxic to microbes (Zeng and Sabra 2011). Engineering an aerobic glycerol to PDO pathway may overcome this issue.

Market Forces/Drivers: Why this Bioproduct?

In one of the clearest examples in the chemicals market, bio-based PDO has been shown to have the advantage over the petroleum-based process. Petroleum-based PDO was an earlier entrant to the market by several years and quickly faded away as the bio-based product went on the market. This suggests that bio-based PDO was less costly to produce. One reason for lower costs could be due to lower energy consumption. DuPont Tate & Lyle Bio Products have stated that bio-based PDO consumes 40% less energy and produces 40% less greenhouse gas emissions compared to the petroleum-based product (DuPont Tate and Lyle Bio Products 2015). These energy and emissions saving were also supported by an independent life-cycle analysis of PDO production from glucose (Urban and Bakshi 2009). Similarly, Sorona has sustainability benefits because of its bio-PDO content. According to DuPont Tate & Lyle, Sorona has 63% less carbon dioxide emissions when compared to nylon 6 (DuPont 2015).

Another area of expansion for bio-based PDO is in consumer products. PDO is currently found in concentrated laundry detergents and spray cleaners produced by Method brand, a naturally derived, biodegradable cleaning products company. PDO has further room to grow in the household products market with potential uses as solvents, stabilizers, and enzyme carriers. As highlighted recently by Simon Herriott, DuPont's global business director for biomaterials, "mainstream consumers are increasingly concerned about the impact their own personal actions have on the environment." He further adds, "we're at an inflection point between the green pioneers and major mainstream formulators" (McCoy 2015d).

Growth is expected to be firm for PDO although some market analyses have aimed high. One estimate has suggested that PDO for use in the production of PTT could reach 225,000 metric tons by 2020 (Corma, Iborra, and Velty 2007). This would double today's demand in 5 short years. As mentioned above DuPont is expecting a more modest 4%–7% CAGR in the near term (Nielson 2014).

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

Glycerol is an abundant byproduct of biodiesel production. Researchers have investigated using crude glycerol for biodiesel to produce PDO. Microbes from the genera *Klebsiella, Citrobacter,* and *Clostridium* produced PDO with productivities up to 2.75 g/L/h and molar yields up to 0.63 (Tang et al. 2013).

METabolic EXplorer recently announced a joint venture with UPM to produce 1,2-propanediol (monopropylene glycol) by fermentation of second generation cellulosic sugars (Metabolic Explorer 2015a). METabolic EXplorer is in the process of modifying the fermentation strain from their sucrose-based 1,2-propanediol process to use cellulosic sugars. METabolic EXplorer is also interested in producing PDO. If their work on 1,2-propanediol from cellulosic sugars is successful, it suggests that they may be able to complete analogous work on PDO from cellulosic sugars.

DOE funded research with DuPont to support the development of the Integrated Corn Biorefinery (ICBR) concept (DOE 2006). The ICBR was envisioned to convert sugars from starch and cellulosic sources to fuel (e.g., ethanol and chemicals [PDO]) (ORNL 2011). Former U.S. Secretary of Energy Samuel W. Bodman was at the opening ceremony of the DuPont Tate& Lyle PDO plant: "It's encouraging to see industry team up to make incredible advances in bio-based technology, building upon the Department of Energy's efforts to reduce our reliance on imported oil, aggressively confront climate change, and help maintain our nation's competitive edge in the global marketplace" (Tate&Lyle 2009).

Propylene Glycol

Propylene glycol (Figure 27), also known as 1,2-propanediol, propane-1,2-diol, and monopropylene glycol, is a viscous, colorless, odorless liquid that does not evaporate (nonvolatile) at room temperature and is completely soluble in water (DOW 2013). PG is safe for human consumption, and therefore is used in the production of consumer products such as antiperspirants, suntan lotions, eye drops, food flavorings, and bulking agent in oral and topical drugs (ADM 2015c). Industrial grade propylene glycol (PGI) is used in the production of unsaturated polyester resins for end use markets such as residential and commercial construction, marine vessels, passenger vehicles, and consumer appliances (IHS 2014b). PG is also used as an engine coolant and anti-freeze in place of ethylene glycol, and in the airline industry as an airplane and runway deicer. In liquid detergents, PG serves as a solvent, enzyme stabilizer, clarifying agent, and diluent (ADM 2015e). Conventional PG has been produced by hydrating propylene oxide (PO), although bio-PG can be produced by hydrogenolysis of glycerin over mixed-metal catalysts, or hydrocracking of sorbitol. A primary driver of bio-PG production is profitable disposition of excess glycerin coproduct of biodiesel production. Companies pursuing bio-PG in the U.S. include ADM, Ashland and Cargill (Grand View Research 2013). International companies pursuing bio-PG include BASF, Oleon, Global Bio-Chem Technology Group (ICIS 2012b), and METabolic EXplorer (Metabolic Explorer 2015b). The ADM bio-PG process is on the list of USDA BioPreferred Intermediate Feedstocks (USDA 2015b).

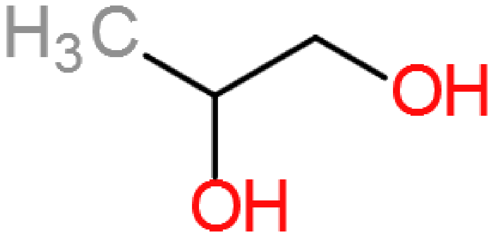

Figure 27. The structure of propylene glycol

Production from Petroleum

Historically, PG has been produced by hydrating propylene oxide (Pavone 2009). Hydration occurs with a large excess of water at reactor conditions of 120°C–190°C and 21 atm. A product mixture of mono-, di-, and tri-propylene glycols is produced. Typical product distribution is 90% PG and 10% coproducts. Excess water is removed in multi-effect evaporators and drying towers. The glycols are then purified using high vacuum distillation (Murphy 2000).

Propylene oxide, the primary feedstock, has historically been produced by the peroxidation of propylene using co-feeds of either ethylbenzene (EB) or isobutene (iC4). When EB is used, PO is produced with styrene monomer coproduct. When iC4 is used, PO is produced with tertiary butyl alcohol (or sometimes MTBE) coproduct (Pavone 2007). PO can also be produced via chlorohydrin chemistry, where chlorine, propylene, and water are combined to make propylene chlorohydrin, which is then reacted with an inorganic base to yield propylene oxide (Murphy 2000). Recently, a new plant has been commissioned by SK Chemicals to avoid coproduct formation by using hydrogen peroxide as the oxidizing agent (Pavone 2009). Figure 28 presents a block flow diagram of the chlorohydrin process to produce propylene oxide, followed by hydration of propylene oxide to produce propylene glycol.

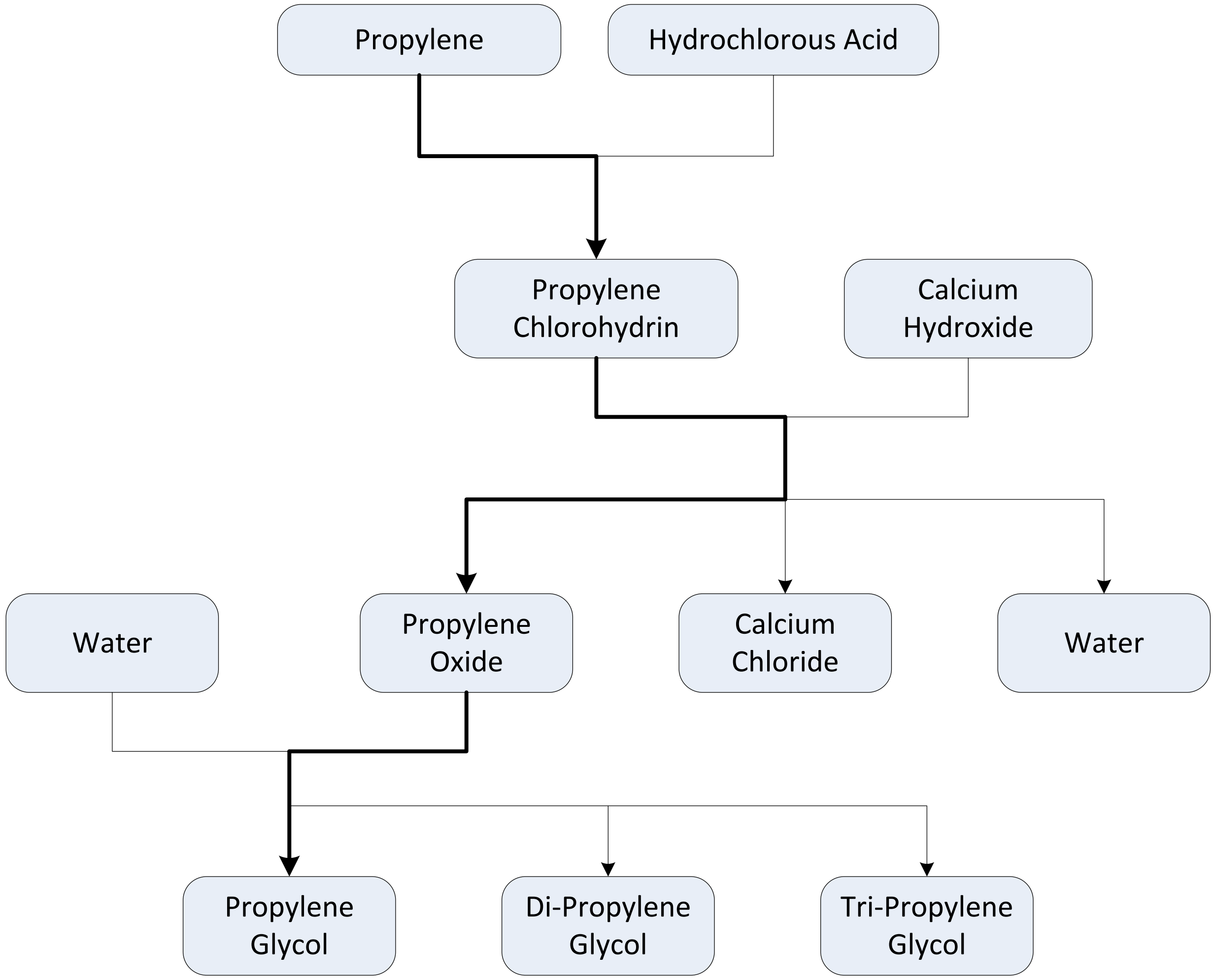

Figure 28. Block flow diagram of chlorohydrin process to produce propylene oxide from propylene, followed by hydration of propylene oxide to propylene glycol

Propylene feedstock is typically obtained as a coproduct of refinery catalytic cracking process used to make gasoline or as a coproduct of steam cracking of ethane in the production of ethylene. On-purpose production is possible via propane dehydrogenation (PDH) (American Chemistry Council 2007).

Consumption and End Products

PG is unique among glycols in that it is safe for human consumption. PG intended for human use or consumption is designated USP grade (Murphy 2000). USP-grade PG has a purity of 99.5% or greater and must comply with USP standards. Non-USP-grade PG is designated as industrial grade (ADM 2015b).

USP-grade PG is used in the fragrance, cosmetics, and personal care industries as an emollient (softener) in products such as antiperspirants, suntan lotions, shaving creams, eye drops, and contact lens solutions. In the food and flavorings industry PG keeps baked goods soft and serves as a solvent for food colorants and flavor extracts. In semi-moist dog food, PG functions as a solvent, stabilizer, preservative, energy source, and humectant. In pharmaceutical application, PG is used as an excipient (bulking agent) or as a solvent in oral and topical drug products (ADM 2015c).

PG is used in the production of unsaturated polyester resins for end use markets such as residential and commercial construction (e.g., building panels, bathroom components, fixtures, corrosion resistant tanks, and ducts), marine vessels (boats), passenger vehicles, and consumer appliances. This is the largest end product application for PG and account for consumption of about 19% in the US, 39% in Western Europe and 80% in China (Landress 2012).

PG is used as an engine coolant and antifreeze in place of ethylene glycol. It is also used in the airline industry as an airplane and runway de-icer due to its biodegradability, low freezing point, low flammability, and ability to decrease the freezing point of water. The low toxicity of PG makes it an ideal heat transfer fluid for machinery in food and consumer products applications. Water-based architectural coatings incorporate PG because it is fully miscible with water and improves application properties by adjusting drying time and aiding in freeze/thaw characteristics. In liquid detergents, PG serves as a solvent, enzyme stabilizer, clarifying agent, and diluent (ADM 2015a).

As of 2013, global PG production grew 8% year over year to about 2.2 million metric tons, while global production capacity was estimated at about 2.8 million metric tons (not actual production). The worldwide PG market is gradually shifting to Asian countries, especially China (Merchant Research and Consulting 2014). The overall PG market is expected to grow at about 4.5% annually in the coming years, with global annual production expecting to reach 2.56 million metric tons (actual production) in 2017 (Merchant Research and Consulting 2014) .

The US is the largest consumer of PG followed by Western Europe, China, and Latin America (IHS 2014b), although consumption in China is expected to increase production and consumption at a fast pace, at least in the near future (Asia Market Information & Development Company 2015). World consumption of propylene glycol in 2013 is presented in Figure 29.

Top producers in the world PG market include Dow, Lyondell Chemical Company, Global Bio-Chem Technology Group, INEOS Oxide, Nihon Oxirane Co., Sinopec Zhenhai Refining & Chemical Company, Archer Daniels Midland Co., SK Chemicals, Shell Eastern Petroleum (Pte) Ltd., Arrow Chemical Group Corp., BASF, Repsol YPF, and Huntsman Corporation (Merchant Research and Consulting 2014).

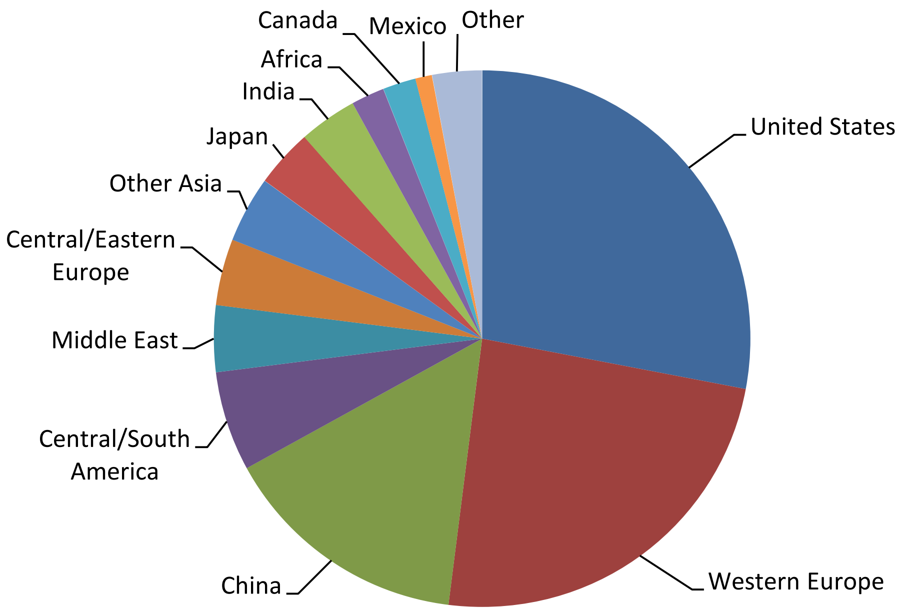

Figure 29. World consumption of propylene glycol in 2013 (IHS 2014b)[7]

USDA BIOPREFERRED AND EPA SNAP

BioPreferred is a program managed by the USDA to increase the purchase and use of bio-based products. The program was created by the 2002 Farm Bill and reauthorized in the Agriculture Act of 2014 (Young 2008, USDA 2014). The goal of the program is to create jobs by opening new markets for farm commodities (USDA 2015c). There are two parts to the program: (1) mandatory purchasing by federal agencies and their contractors, and (2) a voluntary labeling initiative for bio-based products. The USDA has identified 97 categories of bio-based products which have purchasing requirements (USDA 2015a, Golden et al. 2015). The USDA provides tools and training to assist with meeting the purchasing requirements. The labeling initiative is intended to help consumers find information on the bio-based content of products. Manufacturers' claims related to bio-based content are certified by a third party and monitored by the USDA.

SNAP is a long standing program administered by the EPA to evaluate and regulate functional replacements for ozone-depleting chemicals (EPA 2015b). The program began in 1994 to support the ozone protection provisions of the Clean Air Act (EPA 2015a, 2014b). The SNAP program has reviewed substitutes for eight industrial sectors: Refrigeration & Air Conditioning, Foam Blowing Agents, Cleaning Solvents, Fire Suppression & Explosion Protection, Aerosols, Sterilants, Tobacco Expansion, and Adhesives, and Coatings & Inks.

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[7] Reproduced with the permission of IHS Chemical.

Both programs are the result of federal regulations. BioPreferred is focused on increasing the adoption of bioproducts in particular. SNAP is focused on improving air quality. If a bioproduct has the right properties, then it can be listed as a SNAP alternative although promoting bioproducts is not the primary intent of the program.

A number of recent reports have reviewed U.S. policy and regulations toward the production of fuels and chemicals from biomass and are included as references here (US White House 2012, OECD 2014, Spaeth 2014, Golden and Handfield 2014, Golden et al. 2015, Bioenergy Technologies Office 2015).

Price History and Volatility

No publicly available price index or historical prices could be found for propylene glycol, although the price of PG is a function of the price of propylene, the primary feedstock for PG production:

> Whichever historic route is taken, PG production economics are dominated by the cost of the basic feedstock propylene. Produced from either natural gas liquids or refinery naphtha, propylene prices have averaged $1,000/mt [metric ton] over the past three years, and PG market prices have been $1,500/mt during the same period. During the mid-2008 crude oil price run up, with naphtha prices exceeding $1,000/mt, market prices for both ethylene and propylene averaged approximately $1,500/mt, driving PG market prices to $2,000/mt (Pavone 2009).

The PG price appears to be consistently $500/metric ton above the propylene price. Most propylene is a byproduct of refinery operations, and propylene prices are a strong function of crude prices (Kulikowski 2014, Yeo 2016).

PG prices are therefore a strong function of propylene and crude oil prices, although the drivers for propylene price may be changing. Excess U.S. propylene supply in the 1990s was a result of high gasoline demand, but U.S. demand for gasoline has slowed, partly as a result of mandatory ethanol blending into gasoline (George 2014). Propylene is also a byproduct of ethylene production from naphtha. Some ethylene production has recently shifted to production from ethane (George 2014), which results in less propylene byproduct (Iyer 2015). Also, the dominant use for propylene is producing polypropylene (ICIS 2010), for which demand is expected to increase over the next decade (Platts 2014). As a result, on-purpose propylene production from propane using PDH should help meet most of the expected demand (Iyer 2015, George 2014, Platts 2014). In the next few years, new PDH capacity is expected to come online in the United States (Platts 2014, Iyer 2015, George 2014) and Asia (Platts 2014, George 2014), which is expected to produce a PDH-induced price ceiling on propylene (George 2014).

Economic influences on demand for PG may also affect prices. For example, production of unsaturated polyester resins dropped by 22% per year in the United States and a total of 7% in Western Europe as a result of the decline in the construction and industrial markets during 2008–2009, although production in both regions recovered to some extent during 2010–2011 (IHS 2014b). Bio-PG supply is not yet significant enough to affect the selling price of PG, therefore the selling price of bio-PG tracks the selling price of conventional PG (Zacher 2015).

Current U.S. Market Status

The United States produces about 30% of the global supply of PG (Merchant Research and Consulting 2014), or about 700,000 metric tons per year. The United States consumes about the same proportion of global consumption (IHS 2014b). ADM owns a facility in Decatur, Illinois, with capacity to produce 100,000 metric tons per year of propylene glycol from glycerin.

In the United States the major end-products of propylene glycol are consumer products such as cosmetics, pharmaceuticals, personal care, and food products (24%), functional fluids such as antifreeze and de-icer (24%). Unsaturated polyester resins (20%) and liquid detergents (17%) are also major end products.

The U.S. markets exhibiting the greatest growth potential are functional fluids and personal care products. Growth prospects in Western Europe appear strong for food, personal care, and pharmaceutical usage. In the Japanese segment, the best growth potential is cutting oils for silicon wafer production (IHS 2014b).

Production from Renewable Sources

The most common method for producing bio-PG is hydrogenolysis of glycerin over mixed-metal catalysts (Figure 30). Several catalyst combinations have been evaluated, such as Pt-Sn-SiO_2 (Barbelli, Santori, and Nichio 2012), Cu-Zn-Al_2O_3 support (Wang and Liu 2014), and Cu-Zn-Cr-Zr (Sharma, Kumar, and Dalai 2014). There are several reaction mechanisms in literature that propose more complicated pathways than simple hydrogenolysis. Some pathways include intermediate compounds such as acetol (Dasari et al. 2005, Meher et al. 2009, Chiu et al. 2008) and glyceraldehyde (Dasari et al. 2005) that often remain as coproducts.

Glycerin is a three-carbon molecule with a hydroxyl group attached to all three-carbon atoms. Propylene glycol and water are produced when one of the terminal hydroxyl radicals is removed by hydrogenolysis. If the hydroxyl radical on the center carbon atom is removed, the result is 1,3-propanediol and water. If hydrogenolysis of the C-C bonds is targeted, the resulting products are ethylene glycol and methane or methanol (Pavone 2009, Dasari et al. 2005, Shuai Wang 2013). Reaction conditions such as temperature, hydrogen partial pressure, catalyst formulation, and catalyst weight percent determine which product is favored, although whichever product is targeted often contains the expected product in addition to small amounts of intermediates and non-targeted products.

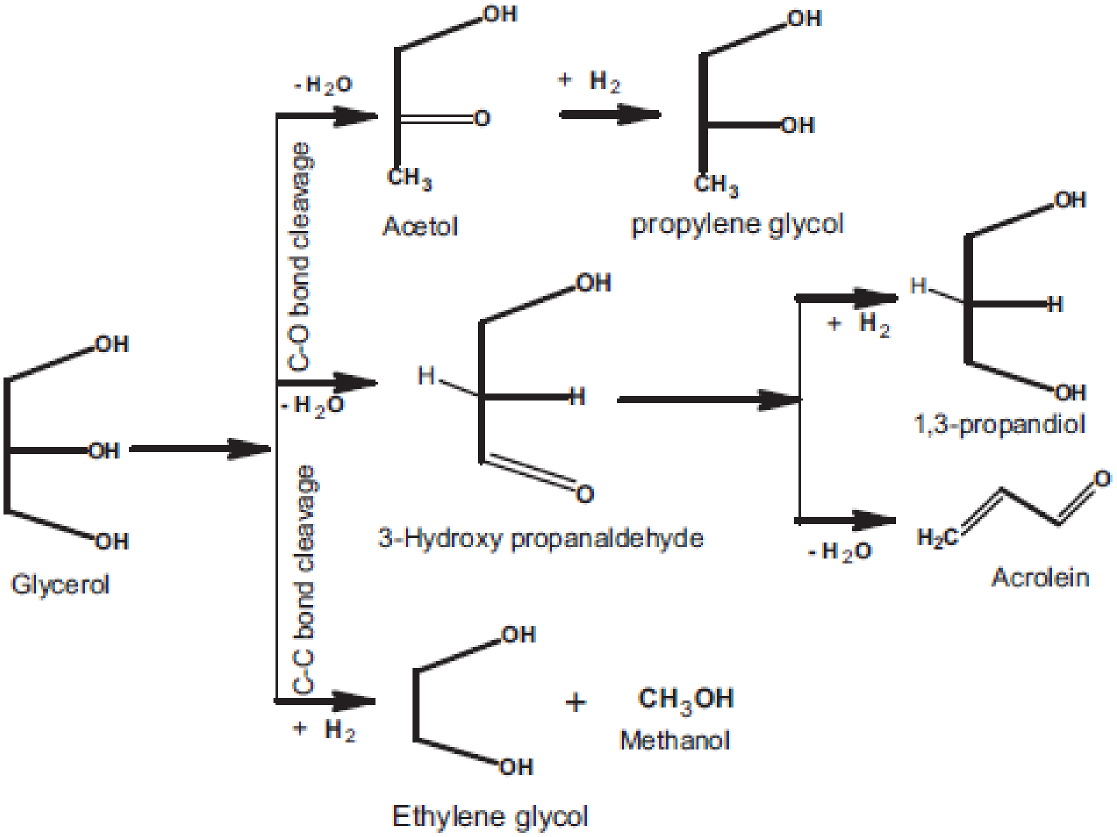

Figure 30. Hydrogenolysis of glycerin (glycerol) to various products (Sharma, Kumar, and Dalai 2014)[8]

Results from a multitude of experimental reaction conditions and catalyst formulations have been published over the last decade. Overall, glycerin conversion to products or intermediates of 80%–90% are achievable (Sharma, Kumar, and Dalai 2014, Dasari et al. 2005), although conversions above 90% and complete conversion are possible if variables such as catalyst loading and hydrogen pressure are optimized (Sharma, Kumar, and Dalai 2014). Likewise, selectivity of 80%–90% to propylene glycol is achievable (Sharma, Kumar, and Dalai 2014, Barbelli, Santori, and Nichio 2012, Dasari et al. 2005), and selectivity above 90% has been reported is some cases (Sharma, Kumar, and Dalai 2014, Wang and Liu 2014, Chiu et al. 2008). Most literature sources report optimum glycerin conversion at reaction temperatures ranging from 200°C to 260°C (Sharma, Kumar, and Dalai 2014, Chiu et al. 2008, Barbelli, Santori, and Nichio 2012, Dasari et al. 2005). Hydrogen partial pressures of 5 to 15 atm minimize the cumulative amount of byproducts that result from hydrocracking versus dehydration side reactions, although the optimum pressure is likely a function of temperature (Chiu et al. 2008). Other literature sources report optimum hydrogen partial pressures of 14 atm (Meher et al. 2009),

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[8] Reprinted from A*pplied Catalysis A: General*, 477, Rajesh V. Sharma, Pardeep Kumar, Ajay K. Dalai, "Selective hydrogenolysis of glycerol to propylene glycol by using Cu:Zn:Cr:Zr mixed metal oxides catalyst," 147-153. Copyright (2014), with permission from Elsevier.

20 atm (Dasari et al. 2005), and 40 atm (Sharma, Kumar, and Dalai 2014). In much of the published literature, experiments were conducted using aqueous feed ranging from 25 to 100 wt% glycerin. Generally, more aqueous glycerin (lower wt%) results in better glycerin conversion and propylene glycol selectivity (Sharma, Kumar, and Dalai 2014, Chiu et al. 2008, Dasari et al. 2005) most likely as a result of lower viscosity or higher catalyst to reactant ratio (more active catalyst sites to convert glycerin to PG) (Sharma, Kumar, and Dalai 2014). Catalyst concentrations (weight of catalyst/weight of glycerin) has also been studied, with concentrations of 3 to 4 wt% resulting in highest glycerin conversion (Sharma, Kumar, and Dalai 2014) and 5 wt% resulting in optimum PG selectivity (Meher et al. 2009), although optimum catalyst loading is most likely dependent on catalyst formulation.

Pacific Northwest National Laboratory (PNNL) developed a process using rhenium-promoted catalysts. The PNNL technology was eventually licensed to ADM for scale-up and commercialization (Holladay, White, et al. 2007). Reaction conditions are not disclosed, although ADM describes the process as high-temperature and high-pressure (ADM 2015b). The ADM process extracts crude vegetable oil from soybeans or canola. The crude vegetable oil is further processed into refined vegetable oil, which is transesterified to crude biodiesel and crude glycerin. The crude glycerin is further processed through several evaporation and distillation steps into a refined, kosher, USP-grade glycerin. This refined glycerin is either sold into the market or processed into propylene glycol. The propylene glycol is further distilled into an industrial-grade or a USP-grade propylene glycol. In addition to manufacturing propylene glycol from glycerin, the ADM facility has the capability to manufacture propylene glycol from sorbitol, a corn-derived sugar alcohol. The plant startup was 2011 in Decatur, Illinois, and has an annual production capacity is 100,000 metric tons (ADM 2015d).

The ADM process is the only glycerin-to-PG facility located in the United States. Belgium-based oleochemical firm Oleon operates a glycerin-to-PG facility. The glycerin feed is a coproduct of biodiesel and oleochemical operations that use animal fats and vegetable as feedstock. Germany-based BASF developed and licensed the bio-based PG production process and supplies the catalysts. The facility was started up 2012 in Ertvelde, Belgium, and has an annual capacity of 20,000 metric tons (ICIS 2012b).

The only other bio-PG facility found in a literature search is a 200,000 metric tons per year plant operated by Global Bio-Chem in Jilin Province, China (ICIS 2012b). The Global Bio-Chem process is corn-based and uses sorbitol as feedstock. Glucose from a wet-milling process is hydrogenated over a metal catalyst to produce sorbitol. The sorbitol is then fed to a hydrocracking process, where it is reacted with hydrogen at high pressure and high temperature over a metal catalyst to crack it into PG, mono-ethylene glycol, and butanediol. The mix of products is then fed to an evaporation and separation plant where water is removed and glycols are separated into pure products. The process produces about 50%–60% PG, 25% ethylene glycol, and 25% 1,2- and 2,3-butanediols and coproducts (Global Bio-Chem 2015). Interestingly, Global Bio-Chem and ADM have partnered to develop a catalyst for producing glycerin from carbohydrates (SpecialChem 2013). A separate description of the bio-PG from sorbitol process, along with a discussion of health and safety concerns of USP-grade PG in consumer products is presented by Rigano and Andolfatto (Rigano and Andolfatto 2013).

METabolic EXplorer, a French company, lists bio-PG from a fermentation process among its product portfolio (Metabolic Explorer 2015b), but has not announced commercialization of a bio-PG facility or approval of its bio-PG product from the FDA.

A literature review found only one cellulosic route to PG: a process discovered by Walter Trahanovsky at Iowa State University that was intended to convert cellulose to glucose but produced glycol byproducts as well. Combining cellulose with alcohols and heating to about 300°C and 150 atm produced the expected alkyl glucoside and levoglucosan derivatives, but 35% of the product was a mixture of propylene glycol and ethylene glycol (Schaefer 2010). No record of the finding being patented or commercialized could be found online.

Data Gaps

The most significant data gaps encountered in this market analysis of bio-PG are the production cost of the glycerin-to-PG process and the selling price of PG. Production costs are either closely-held company secrets, as in the case of the ADM glycerin-to-PG facility, or may be available for a fee from consulting firms (Pavone 2007). As for PG pricing, no pricing index exists (like common refinery products such as naphtha or propylene), although it is suggested that the price can be inferred as approximately $500/metric ton above the price of propylene (Pavone 2009).

Market Forces/Drivers: Why this Bioproduct?

The future expansion of bio-based PG production will depend on the price and availability of low-cost glycerin, which is in turn linked to the development of the biodiesel industry (Jong, Higson, et al. 2012). Another consideration is the selling price of PG, which is dictated by conventional PG selling prices (Zacher 2015). Conventional PG selling price is driven primarily by two factors: (1) propylene selling prices, which are often a function of crude oil prices, and (2) selling prices of other propylene derivatives, such as polypropylene.

Essentially, the economic viability of bio-PG from glycerin is dictated by glycerin market price versus propylene market price (Pavone 2009). As long as glycerin market prices are significantly higher than propylene monomer market prices, there is no compelling economic reason for making PG from glycerin. Biodiesel though, has changed the economics. Since 10% of the production of conventional biodiesel (methanol esterification of fatty acid) represents a glycerin byproduct, the conventional markets for glycerin are well satisfied by the conventional sources of glycerin (from soap and surfactant manufacturing). As the market price of glycerin changes from being more expensive than propylene to less expensive, it makes sense that industrial routes to PG from glycerin might be economically attractive (Pavone 2009).

At current market prices, biodiesel production makes economic sense only when subsidized by government. Without biodiesel, there is no discount-priced glycerin feedstock for making PG. Additionally, biodiesel can be produced by the direct hydrogenation of natural fatty acids, which produces a propane byproduct rather than a glycerin byproduct. If biodiesel production shifts from methanol esterification toward direct hydrogenation the excess glycerin supply may dry up (Pavone 2009).

Additionally, the ADM bio-PG process is on the list of USDA BioPreferred products (USDA 2015b) under the category “intermediate feedstocks,” making it subject to mandatory federal purchasing requirements. Additional glycerin-to-PG facilities would most likely be certified under the BioPreferred program.

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

The glycerin-to-PG process takes advantage of excess glycerin supply created by the government biodiesel subsidies. The process can also be used as additional justification for continued support or expansion of biodiesel production incentives, as renewable uses for byproducts can be viewed as secondary or second-order benefits.

The PNNL glycerin-to-PG technology licensed to ADM was initiated through Laboratory Directed Research and Development funds, which was followed by two separate Cooperative Research and Development Agreements with cost-sharing from DOE’s Office of Energy Efficiency and Renewable Energy, the National Corn Growers Association, ADM, and others. The process decreases greenhouse gas emissions by 61% compared with oil-derived sources. In addition, the ADM Decatur, Illinois, facility was reported to have created 140 jobs (DOE 2015).

Succinic Acid

Succinic acid (Figure 31) is a dicarboxylic acid that can be produced from petroleum or biomass. The current market for petroleum-derived succinic acid is small with a primary focus on specialty chemicals. The projected market for biomass-derived succinic acid is large, however, with succinic acid as a possible precursor for the synthesis of high-value products derived from renewable resources including commodity chemicals, polymers, surfactants, and solvents (Adsul et al. 2011). Due to the large market potential for commercial-scale succinic acid, production facilities have started operation in the past three years utilizing biomass feedstocks with a combined capacity of 55,000 metric tons/year and if all announced projects are completed within the next three years, a total of 140,000 metric tons/year of renewable succinic acid will be available worldwide. A number of additional facilities are planned and the future worldwide production capacity of succinic acid is projected to be more than 400,000 metric tons/year.

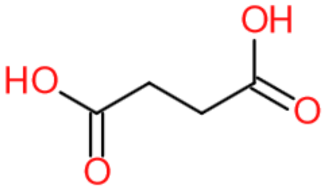

Figure 31. The chemical structure of succinic acid ($C_4H_6O_4$)

Production from Petroleum

The primary route for the production of succinic acid from petroleum is through the hydrogenation of maleic anhydride or maleic acid (Figure 32). Maleic anhydride and maleic acid are manufactured from the oxidation of n-butane, a direct product from petroleum refining or natural gas processing (Wittcoff, Reuben, and Plotkin 2012b).

Current petroleum-based succinic acid manufacturers include: DSM; Israel-based Gadiv Petrochemical Industries; Japanese companies Mitsubishi Chemical Corporation, Kawasaki Kasei Chemicals, and Nippon Shokubai; numerous producers in China including Anqing Hexing Chemical and Anhui Sunsing Chemicals; and smaller producers in India (de Guzman 2012c).

Consumption and End Products

The primary applications for succinic acid include the production of agricultural chemicals, coatings and inks, corrosion inhibitors, solvents, detergents, metal plating, and biodegradable polymers (2014b). As reviewed in more detail below, the projected markets for succinic acid are much larger as it has been identified as a potential platform chemical with numerous pathways toward higher value products, including a route for replacing petroleum-derived 1,4-butanediol, which has a current market demand of more than 2 million metric tons/year (de Guzman 2012c, Werpy, Holladay, and White 2004, Bozell and Petersen 2010).

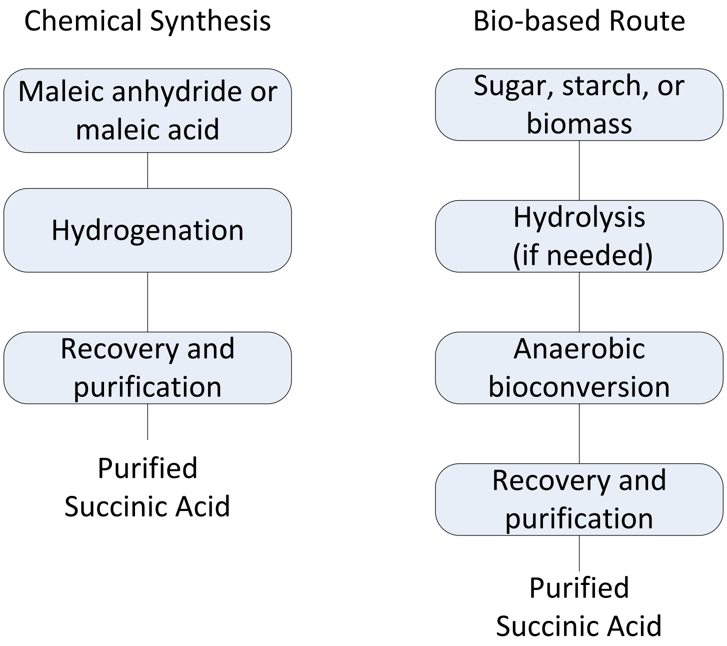

Figure 32. Overview of succinic acid production pathways from petroleum and renewable feedstocks

Price History and Volatility

Information on the historic price of succinic acid is limited. Recent market prices for petroleum-derived succinic acid are reported to range between $6,000 and $9,000/metric ton (The National Non-Food Crops Centre 2013).

Current U.S. Market Status

The world market for succinic acid in 2009 was reported to be 30,000 metric tons with 5% of the market being produced from bio-based feedstocks (de Jong et al. 2012b). The market for succinic acid has varied from 30,000 to 50,000 metric tons with an expected growth rate of approximately 18% from 2011 to 2016 (de Guzman 2012c, The National Non-Food Crops Centre 2013, Markets and Markets 2012). Bio-derived succinic acid production is projected to grow as new facilities come online, such that by 2015 two-thirds of the estimated 90,000 metric tons per year produced globally will be bio-derived (de Jong et al. 2012b). As recently reported by Sven Theysohn, senior manager of succinic acid for BASF Future Businesses, "double digit growth rates are expected in the next five years" and "we see its main impact in new downstream segments like biodegradable polymers" (de Guzman 2012c).

Production from Renewable Sources

Succinic acid is produced via the biological conversion of biomass-derived intermediates including commodity sugars, glycerol, and lignocellulosic sugars. Commodity sugars are the feedstock for the current and planned commercial-scale processes.

There are five different organizations currently pursuing the commercialization of renewable succinic acid. As summarized in Table 9, it is projected by the end of 2014 that 27,000 metric tons/year of renewable succinic acid capacity will be available. The conversion strategy is similar for each of these processes and relies on biological conversion. Table 9 also highlights the differences of each of these processes in terms of the feedstock supply and the reported organism for production.

Succinity GmbH is a joint venture that began in 2009 between BASF and Corbion Purac to develop routes to succinic acid. The process utilizes a genetically engineered strain of the *Basfia succiniciproducens* bacterium that, based on BASF patents, has the capability of converting either a mixed sugar stream or glycerol to succinic acid. The process also utilizes and fixes CO_2 for the production of succinic acid. A 10,000-metric-ton facility came online in mid-2014 at the Corbion Purac site in Montmeló, Spain (de Guzman 2012c, Succinity 2014, Nexant 2012). A larger 50,000-metric-ton facility was noted in the original joint venture (JV) partnership announcement, but no specifics have yet been reported on the location or timing of this project (Succinity 2012).

BioAmber is a joint venture between U.S.-based DNP Green Technology and the French research consortium Agro-industrie Recherches et Développements, which is the research arm of a French agricultural cooperative. The group developed a succinic acid plant in 2008 in Pomacle, France, with a reported initial plant cost of $27 million and annual capacity of 2,000 metric tons (2008). This process was initially demonstrated in 2010 utilizing a licensed DuPont technology, an *E. coli* for succinic acid production, and an industrial-scale 300 m^3 fermenter (Nexant 2012, Voith 2010). BioAmber has since formed a JV with Mitsui Chemicals to produce bio-derived succinic acid and BDO. The reported agreement includes the initial development of a 50,000-metric-ton facility in the LANXESS facility in Sarnia, Ontario, Canada, and began operation in August 2015 with initial production rates of 30,000 metric tons of succinic acid (Bomgardner 2015a). The JV also includes a reported plan to develop commercial-scale facilities in Thailand, as well as the potential of a larger scale process in either the United States or Brazil (Lane 2011a). BioAmber has developed licensing agreements with Cargill to adopt a yeast microorganism that is reportedly tolerant to low pH environments and able to utilize a range of lignocellulosic feedstocks (Nexant 2012, Jansen and van Gulik 2014).

Unlike other bio-succinic acid producers, Myriant is not a joint venture but has partnered with other firms. In 2009, Myriant and ThyssenKrupp Uhde signed an exclusive alliance to commercialize bio-succinic acid and, by June 2013, the companies had scaled and produced succinic acid from commodity sugar feedstocks at the ThyssenKrupp Uhde site in Leuna, Germany. Myriant continues to scale up their fermentation technology that utilizes a genetically modified *E. coli* for succinic acid production. This strain is also reportedly utilized in the 13,600-metric-tons-per-year facility that came online in Lake Providence, Louisiana, in June 2013. The company reported plans to expand the capacity of this facility to 77,000 metric tons per year by late 2015. Myriant has also entered into agreements with China National BlueStar with the potential of scaling up a 100,000-metric-tons-per year succinic acid production facility in Nanjing, China, but a targeted date has not been announced for this facility (Nexant 2012, Lane 2013b).

Reverdia is a joint venture developed in 2010 between Royal DSM, the global life sciences and materials sciences company headquartered in the Netherlands, and Roquette Frères, the global starch and starch-derivatives company based in France. In 2012 the company successfully started a 10,000-metric-tons-per-year succinic acid production facility in Cassano Spinola, Italy, with a process that utilizes a *S. cerevisiae* yeast strain that is tolerant to low pH fermentation. Based on reported life-cycle assessments from the company, this process has reduced GHG emissions since it generates very little waste (Jansen and van Gulik 2014, Reverdia 2014).

Table 9. Current and Planned Succinic Acid Production Capacity (de Guzman 2012c, Succinity 2014, 2012, Nexant 2012, Lane 2011a, Jansen and van Gulik 2014, Lane 2013b, Bomgardner 2015a)

Company	Annual Capacity (metric tons)	Plant Location	Operational Date	Feedstock	Organism
BASF-Purac (Succinity GmbH)	10,000	Montmeló, Spain	March 2014	Crude Glycerol	*B. succiniciproducens*
BASF-Corbion Purac (Succinity GmbH)	50,000	TBD	TBD	TBD	*B. succiniciproducens*
BioAmber	3,000	Pomacle, France	Full capacity 2012	Commodity Sugars	*E. coli*
BioAmber-Mitsui JV	30,000 (initial), 50,000 (full capacity expansion by 2016)	Sarnia, Ontario, Canada	Online August 2015	TBD – Yeast can utilize lignocellulosic feedstocks	*Candida krusei* (licensed from Cargill)
BioAmber-Mitsui JV	65,000	TBD (USA or Brazil)	TBD	TBD	*TBD*
BioAmber-Mitsui JV	65,000	Thailand	TBD	TBD	*TBD*
Myriant	13,600	Lake Providence, Louisiana	June 2013	Commodity Sugar	*E. coli*
Myriant-Uhde	500 (first year)	Leuna, Germany	June 2013	Commodity Sugar	*E. coli*
Myriant	77,110	Lake Providence, Louisiana	Q2 2015 (planned expansion)	Commodity Sugar	*E. coli*
Myriant-China National BlueStar	100,000	Nanjing, China	TBD	TBD	*TBD*
Reverdia (DSM-Roquette)	10,000	Cassano Spinola, Italy	Q4 2012	Commodity Sugars	*S. cerevisiae*

ADIPIC ACID

Succinic acid is being pursued as a functional replacement for adipic acid in specific applications such as polyurethanes, resins, and plasticizers (Business 2011). However, traditionally petroleum-derived adipic acid is produced in a two-stage process that involves the oxidation of cyclohexane followed by nitric acid oxidation of the intermediate to adipic acid (R. Davis 2013). The later steps of the process have a large impact on the sustainability of the overall process (Pavone 2012). Given the large market size of adipic acid, which in 2012 was reported to be 2.3 million metric tons globally with a projected growth rate of 3%–5% per year (IHS 2012), and the potential to improve the sustainability of the process, a number of companies are pursuing renewable adipic acid.

There are several alternative pathways for adipic acid production from biomass at varying stages of development. The two processes that are reported to be furthest along are being pursued by Rennovia and Verdezyne. Verdezyne biologically converts fatty acids and plant-based oils directly to adipic acid. In 2011 the company announced the production of adipic acid in its pilot facilities and, by 2012, the production of renewable nylon fiber (McCoy 2011, Verdezyne 2015, Lane 2014i). The Rennovia process utilizes heterogeneous catalysis, which first produces glucaric acid through an aerobic oxidation of glucose followed by catalytic hydrogenation to adipic acid (Lane 2015b, McCoy 2014). Utilizing the renewable products, the company has synthesized renewable nylon for further external testing in 2013 (Rennovia 2013). Moreover, Rennovia has partnered with Johnson Matthey Process Technologies to demonstrate the production of glucaric acid in mini-plants and is working to scale up the production to adipic acid (Lane 2015b, McCoy 2014). Based on Rennovia's economic and sustainability analysis, the company has estimated that the cost of production via glucaric acid is roughly 20%–25% below conventional petroleum-based adipic acid and that a 85% reduction in greenhouse gas emissions may be realized (Lane 2014h, Aguilar et al. 2002).

Celexion is utilizing anaerobic routes for the direct conversion to adipic acid from carbohydrates with the technology currently being licensed by BioAmber (Sims 2011, Plastics Today Staff 2011). Royal DSM has also reported adding renewable adipic acid to their chemicals portfolio, with ongoing efforts to move the production to demonstration scales (Business 2011). Genomatica has filed a patent for the production of adipic acid from commodity sugars (Business 2011). The production of adipic acid through intermediates other than glucaric acid is also being considered. Deinove, Myriant, and Amyris have been pursuing the production of muconic acid followed by chemical catalytic conversion to adipic acid, with the majority of these processes having been demonstrated thus far at the bench scale (Lane 2015a, 2014f, Tullo 2011a). Similar routes, utilizing lignin components, have been recently demonstrated at the lab scale at the National Renewable Energy Laboratory (Vardon et al. 2014).

Data Gaps

During the initial public offering (IPO) filings, both Myriant and BioAmber indicated that their technologies would be cost competitive with petroleum at \$45/barrel of oil and \$35/barrel of oil, respectively. Neither company has since reported on the price of succinic acid production (Lane 2011b, 2013a).

Since the original DOE top 10 value-added chemicals report was prepared (Werpy, Holladay, and White 2004), review articles summarizing the microorganisms being pursued for the commercial production of succinic acid have been published. Selected write-ups are referenced in this report for further consideration (de Jong et al. 2012b, Cheng et al. 2013, Song and Lee 2006, Cheng, Zhao, Zeng, Wu, et al. 2012, Cheng, Zhao, Zeng, and Zhang 2012).

From a process standpoint, one of the biggest challenges for the production of organic acids, and in general chemicals production, is the cost associated with separations and purification. Costs of between 50% and 75% of the succinic acid have been attributed to separations (Zeikus, Jain, and Elankovan 1999, Orjuela et al. 2013). Both BioAmber and Reverdia are pursuing organisms with tolerance to low pH conditions to help reduce the cost of separations and, as noted by life-cycle assessment studies performed by Reverdia, to improve the overall sustainability of the process (The National Non-Food Crops Centre 2013, Reverdia 2013).

Market Forces/Drivers: Why this Bioproduct?

The current market for succinic acid is small and petroleum-derived succinic acid has filled niche or specialty chemical needs. For biomass-derived succinic acid, the focus has been on finding a market for bio-succinic acid as a "drop-in" replacement for petroleum-based chemicals with what has been noted as "a more than $30 billion market opportunity" (Lane 2014c). Succinic acid is a potential precursor for the synthesis of high-value products derived from renewable resources including polymers, surfactants, and solvents. As outlined in the top 10 value-added chemicals from biomass report (and replicated in Figure 33), succinic acid may become a platform chemical with the potential to produce a number of large-scale commodity chemicals (Bozell and Petersen 2010, Werpy, Holladay, and White 2004). The current producers of biologically derived succinic acid have reported that numerous agreements and contracts are in place to sell succinic acid for the production of these value-added products. A few of these efforts are highlighted here.

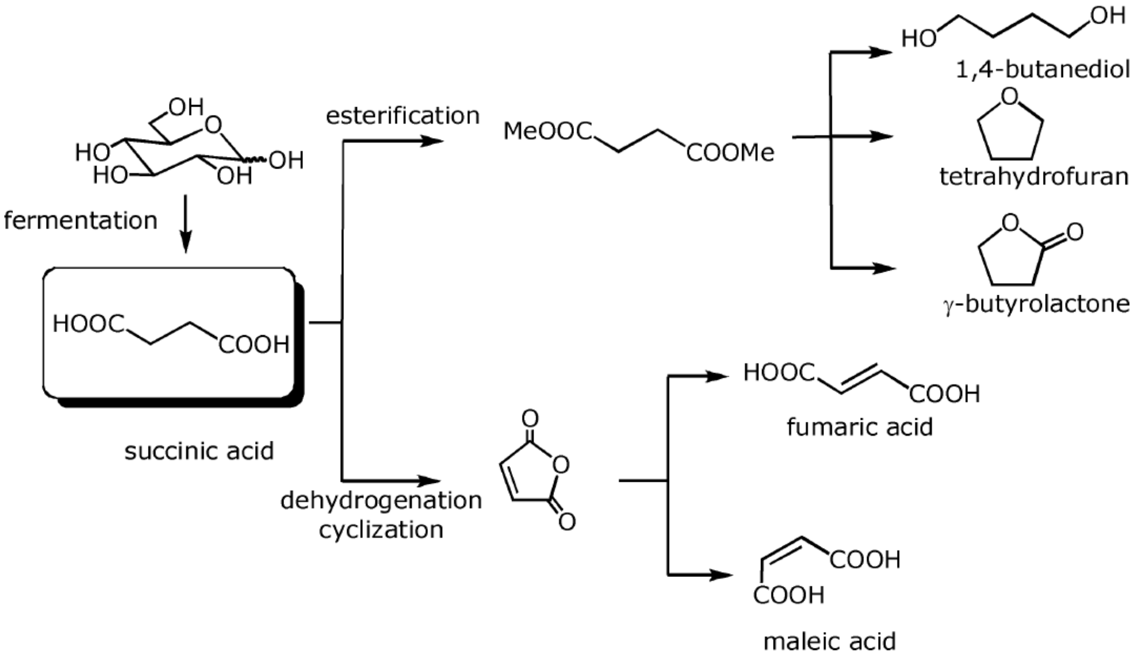

Figure 33. Potential products from a succinic acid intermediate (Bozell and Petersen 2010)[9]

1,4-butanediol: A promising commodity chemical being pursued by both BioAmber and Myriant is 1,4-butanediol. BDO has one of the highest market demands of the potential succinic acid derivatives at more than 2 million metric tons/year (de Guzman 2012c, Bozell and Petersen 2010). BioAmber is working to convert succinic acid to larger scale commodity chemicals. The company recently signed an agreement with Evonik Industries to develop catalysts for making BDO, as well as tetrahydrofuran and γ-butyrolactone, from bio-based succinic acid. BioAmber noted that the catalysts being pursued with Evonik will complement the BDO catalyst technology it licensed from DuPont in 2010 (McCoy 2012). BioAmber has signed off-take agreements with Vinmar International, a Houston-based distribution company, for the purchase of 100,000 metric tons of BDO annually for 15 years and 80,000 metric tons of succinic acid with expansion to 230,000 metric tons of succinic acid per year by 2020 (Bomgardner 2014c). Myriant signed a memorandum of understanding in 2011 with Davy Technologies, a Johnson Matthey company, for the use of succinic acid as a bio-derived feedstock for the production of butanediol, as well as tetrahydrofuran, and γ-butyrolactone. Approximately 25% of the global production of butanediol, tetrahydrofuran, and γ-butyrolactone utilizes a proprietary production process licensed by Davy Technologies (Myriant 2013).

Plasticizers: BioAmber has developed partnerships to develop routes for the utilization of succinic acid, including collaborations with LANXESS for the joint development of phthalate-free plasticizers from succinic acid. The production facility in Ontario, has been built and integrated at the LANXESS site (Tullo 2011c). Myriant is working with OXEA to develop

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[9] Adapted from Bozell and Petersen 2010 with permission of The Royal Society of Chemistry.

phthalate-free plasticizers and in early 2014 supplied commercial-level succinic acid production and testing of these products (Lane 2014f).

Bio-based polymers: Polybutylene succinate (PBS) polymers are being targeted as a replacement for conventional plastics as they can be produced through renewable sources of succinic acid and 1,4-butanediol with potential applications in flexible packaging, agricultural films, compostable bags, and food service ware. PBS is currently being produced at small scales from conventional petroleum-derived precursors but the demand of bio-renewable plastics is expected to increase (de Guzman 2012c). In fact, estimates from BioAmber put this market in the $2 billion range. Currently BioAmber has a joint venture with NatureWorks, named AmberWorks to develop compostable plastics using succinic acid-based polymers such as PBS (Tullo 2012b). PBS is being utilized with PLA to improve the properties of PLA including its flexibility, heat performance, and biodegradability (Tullo 2012b). Both Myriant and Reverdia have also reportedly been targeting the PBS market (de Guzman 2012c).

Other markets: BioAmber has signed agreements with INOLEX for the production of personal care products from succinic acid (2012a). BioAmber is working with Turkey's Flokser to produce Sertex, an artificial leather fabric. This polyester polyol is reported to have 70% renewable content made from succinic acid produced by BioAmber and propanediol (produced by DuPont Tate & Lyle Bio Products) with an estimated market of 150,000 metric tons per year (McCoy 2015c). Reverdia is currently working with Proviron to produce di-methyl succinic acid for use as a solvent and a raw material for fine chemicals such as pigments and UV stabilizers (Lane 2014g).

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

Scale-up of succinic acid is focused on the production of chemicals and is expected to have a limited impact on accelerating hydrocarbon biofuel production.

A number of the succinic acid routes and technologies have been funded by the DOE. The original microorganism that BioAmber utilized in the process facility in Pomacle, was developed in 1995 by DOE and DNP Green Technology's predecessor Applied CarboChemicals (Thayer 2009). Myriant's Lake Providence commercial facility is partially funded by a $50 million cost share cooperative agreement with the DOE, $25 million from the USDA Business & Industry Loan Guarantee Program, as well as a $10 million grant from the Lake Providence Port Commission and the Louisiana Department of Transportation & Development (Lane 2014f).

Xylene (para)

Para-xylene (Figure 34) is used to produce both terephthalic acid and dimethyl terephthalate with both of these chemicals being raw materials for the production of polyethylene terephthalate (PET) fiber and bottles. Major consumers of PET bottles, including Coca-Cola and Pepsi, are supporting efforts to develop renewable bottles on a targeted timeline and by actively funding R&D efforts for the production of renewable PET. The renewable replacements that are currently being developed include a direct replacement for petroleum-derived pX or functional replacements of PET (such as polyethylene furanoate).

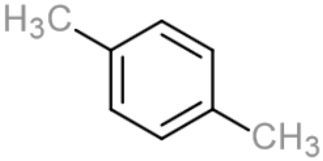

Figure 34. The chemical structure of para-xylene (C_8H_{10})

Production from Petroleum

A block diagram comparing the various routes to pX is shown in Figure 35. The conventional technology for pX production is based on the isomerization and catalytic reforming of mixed xylenes from refinery reformate streams or from pyrolysis gasoline (pygas) (Guo 2012, Mirasol 2014, 2014b).

When petroleum is reformed in a conventional refinery operation, a stream rich in aromatics is produced and available for either blending into gasoline (for high octane fuel) or sent to chemical processing for further conversion and clean-up. Xylene-rich streams are also produced as a byproduct of cracking hydrocarbon feeds (i.e., naphtha/gas oil) for olefin manufacturing, which is often referred to as pygas (Collias Dimitris I. 2014, Burdick 2010). These streams are typically rich in benzene, toluene, and mixed xylenes/aromatics (BTX), as well as other C6, C7, and C8 aromatics with meta-xylene (a low cost coproduct) being the prominent xylene from reformate (Wittcoff, Reuben, and Plotkin 2012a).

High purity pX can be obtained using either crystallization or selective adsorptive separation. Additional processing options employed by some petroleum pX producers to maximize yields include toluene disproportionation and transalkylation. In toluene disproportionation, toluene is converted to both xylenes and benzene, with the production of benzene being undesirable due to challenges downstream in recovery/purification. In transalkylation, an alkyl group from one aromatic is transferred to another aromatic compound maximizing the production of xylenes (2014b, Collias Dimitris I. 2014).

Other petroleum-derived processes have been developed by U.S.-based UOP. The Cyclar process converts propane and butane to pX and benzene (Mirasol 2014, UOP 2014a).

Asia is the top producer and consumer of pX, with China, India, and South Korea accounting for more than 70% of the world production (IHS 2015b). Projections have shown that China alone will have steady market growth for pX reaching an additional 20 million metric tons in demand by 2024 (UOP 2014c, Guo 2012). Despite the pX capacity growth in China predicted to be roughly 1% per year from 2015–2020, China is expected to continue to be a major importer of pX to meet the growing demand from the purified terephthalic acid (PTA) processes that are coming online (IHS 2015b). An additional nearly 5 million metric tons/year is expected to be added by 2014 (10.5 million metric tons were added in 2013) putting the PTA capacity in China at roughly 33 million metric tons/year (Wong 2014). There is uncertainty in the demand for PTA and projections show that PTA will remain oversupplied through 2020. An additional 20 PTA plants are slated to come online between 2013 and 2018 resulting in a total annual production capacity of more than 95 million metric tons (Boswell 2014a). This amount of PTA is much higher than the annual demand of 65 million metric tons expected by 2018. This glut of PTA makes the market very uncertain for pX producers (Boswell 2014a).

The United States is the fourth largest producer of pX worldwide, with BP being the largest producer and consumer in the United States (Mirasol 2014, UOP 2014c). Unlike other chemical producers, BP consumes much of the pX produced in their PTA processes. ExxonMobil is second to BP in the production of pX in the United States and sells all of the pX that is manufactured on the merchant market.

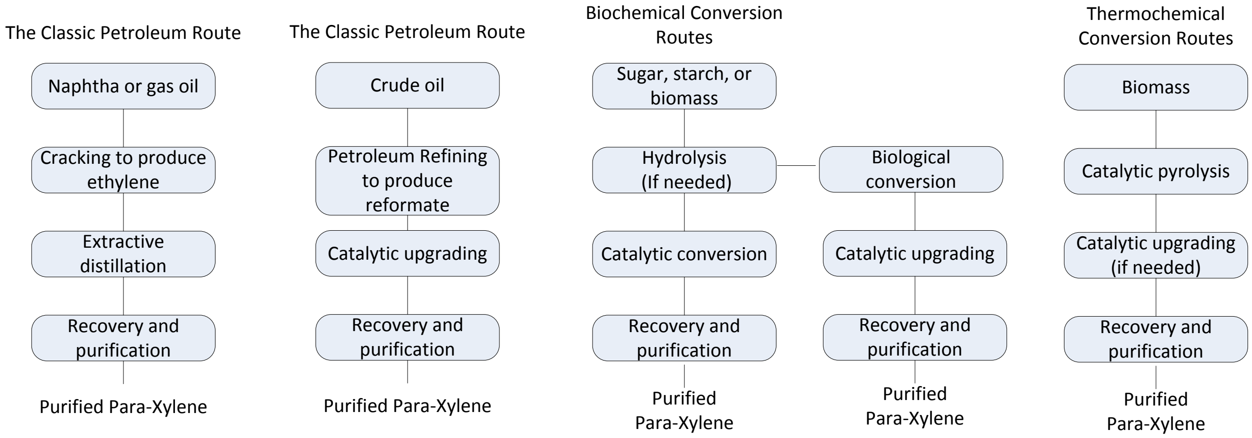

Figure 35. An overview of pX production pathways from petroleum and renewable feedstocks

Consumption and End Products

Para-xylene is primarily used to produce terephthalic acid. It is also a raw material for the manufacture of DMT, di-paraxylene, and herbicides, and it is used in solvents (Mirasol 2014). PET can be produced from the combined conversion of terephthalic acid and mono-ethylene glycol (Komula 2011). DMT can be used to manufacture PET, PBT, and PTT resin (Mirasol 2014).

Approximately 97% of the pX produced is used to manufacture polyesters, with 65% destined for fibers, 27% for PET bottle resin, and the remaining 8% for film and other plastic end uses (Mirasol 2014).

Price History and Volatility

The historic and projected prices for pX are summarized in other sources and have shown prices as low as $200/metric ton in the early 1990s up to over $600/metric ton in the later 2000s (UOP 2014c). The key drivers for the price of pX are the cost of feedstock (mixed xylene/crude) and impacts of the polyester supply chain. The installation of pX processes and capacity expansion is typically cyclical in this industry, with the market experiencing booms and busts that greatly impact producers. The favorable markets in the mid-1990s resulted in the expansion of pX capacity leading to an oversupply by the late 1990s. Worldwide pX production capacity exceeded the demand by more than 4.5 million metric tons per year by 2001, lowering the average capacity utilization to less than 80% (UOP 2014c). Due to the oversupply of pX, margins were tight in the early 2000s and producers were reluctant to expand or build new units. In the meantime, PET demand rose steadily and, by 2005, the surplus had dropped to 1.5 million tons/year. This encouraged producers to again expand capacity. In 2010–2011, demand for pX was weak due to economic drivers and a lack of consumer confidence and spending. Furthermore, the pX market has been soft due to cutbacks in China for pX due to the overproduction of PET fibers used in textile production. Similar price swings seen in the 1990s remain a concern for future pX prices as the market is projected to be long on pX by 2017 if all capacity announced in Asia and the Middle East comes online as planned.

Current U.S. Market Status

The United States is currently a net exporter of both para-xylenes and mixed xylenes providing about 25% of the Asian mixed xylene imports. This a potential challenge for U.S. producers as more pX capacity comes online in China and in the Middle East. With announced projects equating to an increase of roughly 21 million metric tons of para-xylenes between 2013 and 2017, projections show that by 2017 there will be an oversupply of pX. Analysts note that this increased pX capacity will negatively impact both mixed xylene and pX prices as “demand for U.S. material will likely wane” (Allen 2013).

For the developing bio-pX market, there are numerous companies (e.g., Coca-Cola, H.J. Heinz, Toray, and Ford Motor Co.) that utilize PET and are actively funding and supporting the production of renewable pX, which helps to stabilize a very uncertain market.

Production from Renewable Sources

There are numerous processes under development for the production of renewable pX. These routes range from utilizing all of the biomass or portions of the biomass including the carbohydrate and lignin fractions. These strategies span traditional biochemical fermentation, followed by upgrading, thermochemical pyrolysis routes, and hybrid thermochemical/biochemical strategies of catalytic upgrading of sugars.

The companies pursuing the production of renewable pX are developing a wide array of technologies. These pathways either produce pure pX or BTX similar to petroleum-derived reformate for further upgrading to pX. Gevo Inc. and Micromidas are developing processes focused on selective pX production while Virent, Anellotech, and Biochemtex S.p.A. are developing routes toward reformate production. Gevo and Virent have utilized their demonstration-scale facilities and Anellotech has used their pilot facility to produce renewable pX for testing by external consumers and partners.

The process developed by Gevo directly converts isobutanol to pX. Gevo utilizes fermentation to convert a biomass-derived sugar substrate to isobutanol. The Gevo-developed microorganism is reported to be a yeast that can convert both C5 and C6 sugars to isobutanol (Collias Dimitris I. 2014, Bruijnincx and Weckhuysen 2013). The isobutanol is then dehydrated to isobutylene over either a heterogeneous or homogenous catalyst such as sulfuric acid, hydrogen fluoride, solid phosphoric acids, and metal oxides. Using an oligomerization catalyst, the isobutylene is dimerized to diisobutylene, which then undergoes dehydrocyclization producing pX and hydrogen via an alumina-based or silica-based heterogeneous catalyst. Gevo has successfully scaled up this process at its demonstration-scale facility in Silsbee, Texas, which started up in 2013 (Bomgardner 2013c). This facility can produce more than 0.45 metric tons/month of bio-pX. Gevo has developed partnerships with Toray and Coca-Cola with both companies supporting the scale-up of Gevo's process (Coons 2013). In 2011, Toray utilized Gevo's bio-isobutylene to produce renewable PET (Lane 2014a). The partnership between Toray and Gevo includes an agreement by Toray to purchase pX from Gevo. According to the February 2011 IPO filing by Gevo with the U.S. Securities and Exchange Commission, Toray agreed to start purchasing 1,000 metric tons/year of bio-pX from Gevo after 2012 and could potentially increase this agreement to 5,000 annual metric tons within 5 years. The first bio-derived pX was shipped to Toray for further development in 2014 (Lane 2014a, Bomgardner 2014b).

Micromidas is developing a chemo-catalytic route for the direct production of bio-derived pX from various cellulosic biomass feedstocks. According to the company, the "process achieves very high yields, utilizing a 3-step standard chemical conversion process with conventional reactor/separation equipment and configurations. The process is highly flexible, capable of handling a wide variety of waste feedstocks such as OCC [old corrugated containers], rice hulls, empty palm fruit bunches, paper sludge, and wood chips" (de Guzman 2013b). Based on Micromidas patents, pX can be produced either via 2,5-hexanedione or 2,5-dimethylfuran. The 2,5-hexanedione can be produced via dimethylfuran using hydration or other methods. Hexanedione can be reacted with ethylene in the presence of solvents and catalyst to produce renewable pX (Collias Dimitris I. 2014). Micromidas has reported commissioning a pilot plant with a 500 kg/day pX production capacity (de Guzman 2013b).

Virent has developed conversion strategies for the upgrading of solubilized carbohydrate components to renewable pX through a hybrid biochemical and thermochemical process. Its BioForming process takes a stream of solubilized biomass through an aqueous phase reforming (APR) step. In APR, the biomass-derived components are converted in the presence of hydrogen through a series of reactions to reduce the oxygen content of the feedstock via a conversion over heterogeneous catalysts at moderate temperatures (450 to 575 K) and pressures (10 to 90 bar) (Collias Dimitris I. 2014, Komula 2011). These mono-oxygenated species (e.g., alcohols, ketones, and aldehydes) undergo condensation over a modified ZSM-5 catalyst to produce a stream of aromatic rich products, named BioFormate (Komula 2011). Since the product is similar to petroleum-derived reformate, these products can be further upgraded to renewable aromatics (including pX) utilizing the same technologies as in petroleum production. Reports by Virent have stated that the reformate stream is similar to petroleum-derived reformate streams based on analytical techniques (Komula 2011). The work on mixed xylenes began in 2010 and by mid-2011 the company reported the production of pX from plant-based sugars. Also in 2011, Virent and the Coca-Cola Company announced a multiyear joint agreement for the development and supply of BioFormPX. This technology was recognized by ICIS with an award for Best

Innovation for Sustainability (Virent 2014a). Based on Virent reports, the company is targeting near-term commercial production of the BioFormPX with a proposed process scale between 30,000 and 225,000 metric tons/year (Komula 2011). In 2015, the company showcased the production of a plant bottle produced from 100% renewable material at the Coca-Cola pavilion at Expo Milano (Tullo 2015).

Renewable pX is being pursued via a thermochemical route by Anellotech. This pathway utilizes a catalytic fast pyrolysis process originally developed by Professor George Huber at the University of Massachusetts-Amherst and licensed by Anellotech. A range of cellulosic feedstocks can be converted using a single fluidized bed reactor technology in the presence of a proprietary ZSM-5 based catalyst to produce renewable BTX which can be further upgraded to renewable aromatics including pX. In 2013, Anellotech started up a pilot-scale facility in Pearl River, New York, and by mid-2014 produced kilogram amounts of BTX, which were provided to unnamed strategic partners (Anellotech 2014, 2014a).

The production of biomass-derived reformate from lignin feedstocks has been described by numerous companies and one of the leading organizations pursuing this approach is Biochemtex in Tortona, Italy (previously known as Chemtex Italia), which is also a part of the Mossi Ghisolfi Group in Tortona, one of the world's leading producers of PET (Collias Dimitris I. 2014, Plastics News 2012). The Biochemtex process utilizes lignin from the Beta Renewables' lignocellulosic ethanol process. Beta Renewables is a joint venture between Biochemtex, TPG Capital, and Novozymes. This lignin is obtained after a pretreatment process to convert the carbohydrate fraction into monomeric sugars via steam explosion and hydrolysis. Based on the company's patent, lignin is converted in its MOGHI process to BTX at elevated temperatures and pressures in the presence of hydrogen, an elemental catalyst (such as Raney nickel), and potentially a hydrogen donor solvent (Collias Dimitris I. 2014). In 2014, the company announced it would be investing $183 million to develop processes for biomass conversion to fuel and chemicals but was not specific on which pathways would have priority (Scott 2014).

There are other conversion strategies that have been suggested through the patent literature by other companies. For example, a process is described in separate patents by UOP and Toray that produces pX via biomass-derived dimethylfuran (DMF). The process is based on the Diels-Alder cycloaddition of DMF and ethylene followed by dehydration of the resulting bicyclic ether intermediate to pX (Collias Dimitris I. 2014). A process described by SABIC claims the production of pX via use of terpenes such as limonene found in citrus fruits (ICIS 2012a). Further academic institutions continue to develop catalytic routes toward bio-derived pX including University of Massachusetts-Amherst and the University of North Carolina at Chapel Hill (Collias Dimitris I. 2014).

FURAN DICARBOXYLIC ACID

Not only has Coca-Cola been investing in routes toward drop-in replacements for polyethylene terephthalate, but it also has actively funded efforts to develop functional replacement options such as polyethylene furanoate. The production of PET and PEF are similar in that each plastic is produced via a reaction involving ethylene glycol. In contrast, however, PET is produced using a PTA monomer, whereas PEF is produced via FDCA and is a polyfuran (Tullo 2013e, de Guzman 2012b, Jong, Dam, et al. 2012).

Avantium has been working to improve the catalytic production of FDCA from biomass carbohydrates for more than a decade. The company began to construct a pilot facility in 2011 with a capacity of 20 tons per year in the Netherlands (partially supported by a 1 million Euro grant from the Dutch Ministry of Agriculture) and is scaling up the process to a 50,000-ton production facility that is expected to come online in 2016 or 2017 (Bomgardner 2013a, Lane 2010, 2014b, Deligio 2014).

Beyond scaling up the process, Avantium has also worked to address barriers for the adoption of functional replacement chemicals, including testing the performance (including thermal, mechanical, and barrier properties) of the ultimate polymer product relative to PET, obtaining approval for food contact from the European Food Safety Authority, and investigating the impact that PEF would have on the recycling stream when commingled with other plastics (Bomgardner 2013a, Imhof 2012, Whitworth 2014).

Data Gaps

No data is available for renewable pX capital, operating, and product costs.

In 2012, Coca-Cola, Ford, Heinz, Nike, and Procter & Gamble formed a consortium to promote research for developing PET that is 100% derived from renewable raw materials. The consortium published a peer-reviewed journal article reviewing bio-based terephthalic acid technologies (Collias Dimitris I. 2014).

A major economic and technology challenge for producing pX is the separation and purification necessary to achieve final products with adequate purity for commercial applications. Commercial-grade pX targets a purity specification of 99.7% from petroleum, particularly in the production of PET bottles (Komula 2011). The impurities found in biomass-derived products are expected to vary relative to petroleum-derived pX and reformate. With the exception of Virent, which has provided analytical comparisons using a GC trace of the BioForming product versus traditional petroleum-derived reformate streams and has shown similar quality, limited data is available on these impurities or their impact on PTA/PET production (Komula 2011).

Market Forces/Drivers: Why this Bioproduct?

The biggest driver for adoption of renewable pX is the production of PTA, which constitutes roughly 70% of the raw materials to produce PET, with the other component being ethylene glycol.

Since 2009, Coca-Cola has been utilizing PET produced from renewable ethylene glycol, referred to as PlantBottle in the bottles for Dasani brand water. The company, which consumes roughly 16% of the world's PET bottles, has set strategic targets for replacing the components of PET bottles by 2020 including utilizing PlantBottle in all products, as well as introducing renewable PTA into these bottles (Tullo 2012a, Coons 2014a). The decision toward moving to renewable sources was a consideration of the supply chain impacts and cost associated with PET. A recent article on renewable chemicals and Coca-Cola's strategy notes that "when putting together their 2020 plan, Coca-Cola realized it faced increasingly volatile oil prices and that it must protect the trust of its consumers to keep its license to operate" (Coons 2014a). Further, the company has also stated they expect consumers will not pay a premium for renewable products but rather are working with producers of bio-derived pX and PET replacements to scale up these processes and utilize economies of scales to drive down costs and make the PlantBottle cost-competitive with petroleum-derived PET. Otherwise, Scott Vitters, general manager of PlantBottle packaging at Coca-Cola, says this about the current efforts: "I'm not sure that value proposition would have been sufficient enough for us to make that investment" (Tullo 2012a). In fact, Coca-Cola announced in 2012 it had signed development agreements with three companies to develop renewable PTA, including supporting Virent and Gevo for the production of renewable pX and Avantium, which is developing a route toward polyethylene furanoate (PEF), a potential functional replacement for PET (Tullo 2013b, de Guzman 2012b).

In 2012, a consortium was brought together between, Coca-Cola, Ford, Heinz, Nike, and Procter & Gamble to promote research for developing PET that is 100% derived from renewable raw materials (Collias Dimitris I. 2014).

In 2011, Pepsi announced the development of a renewable PET bottle and plans to develop a pilot plant facility by 2012; however, the current status of the project is unclear, as was whether the product was pX or a pX intermediate (de Guzman 2011, Tullo 2011b).

Leveraging to Accelerate Biofuel Scale-Up/DOE Interest

The BioFormate being developed by Virent is a stream commonly blended into high octane gasoline. This product has been blended into a gasoline fuel used by Shell and the Scuderia Ferrari Formula 1 racing team (Komula 2011). Gasoline produced in Virent's BioForming process was recently certified by the EPA for blending of up to 45% (Virent 2014b). Gevo has developed the Silsbee, Texas, facility to be flexible toward final product conversion of isobutanol to either pX or jet fuel (Coons 2013).

GLOBAL COMPETITIVENESS

The global market for polymers and commodity, specialty, and fine chemicals was $1.2 trillion in 2005. The global chemical demand is expected to grow between 3% and 6% per year through 2025. Analysis by the USDA suggests that bio-based products could grow more quickly, increasing from 2% of the market in 2008 to 22% in 2025 (Duncan et al. 2008, Williamson 2010).

A closer look at regional data for chemical consumption is shown in Figure 36. The growth in consumption of chemicals is largely similar between the United States and the European Union. The expected growth in consumption in China is greater across the board. This trend mirrors the differences in gross domestic product (GDP) growth by region. GDP growth in China was 7.4% in 2014 versus 2.4% in the United States (CIA 2013). The higher GDP growth rate for China is expected to continue in the near-term and that trend is reflected in the consumption of chemicals (The World Bank 2015, IHS 2015a).

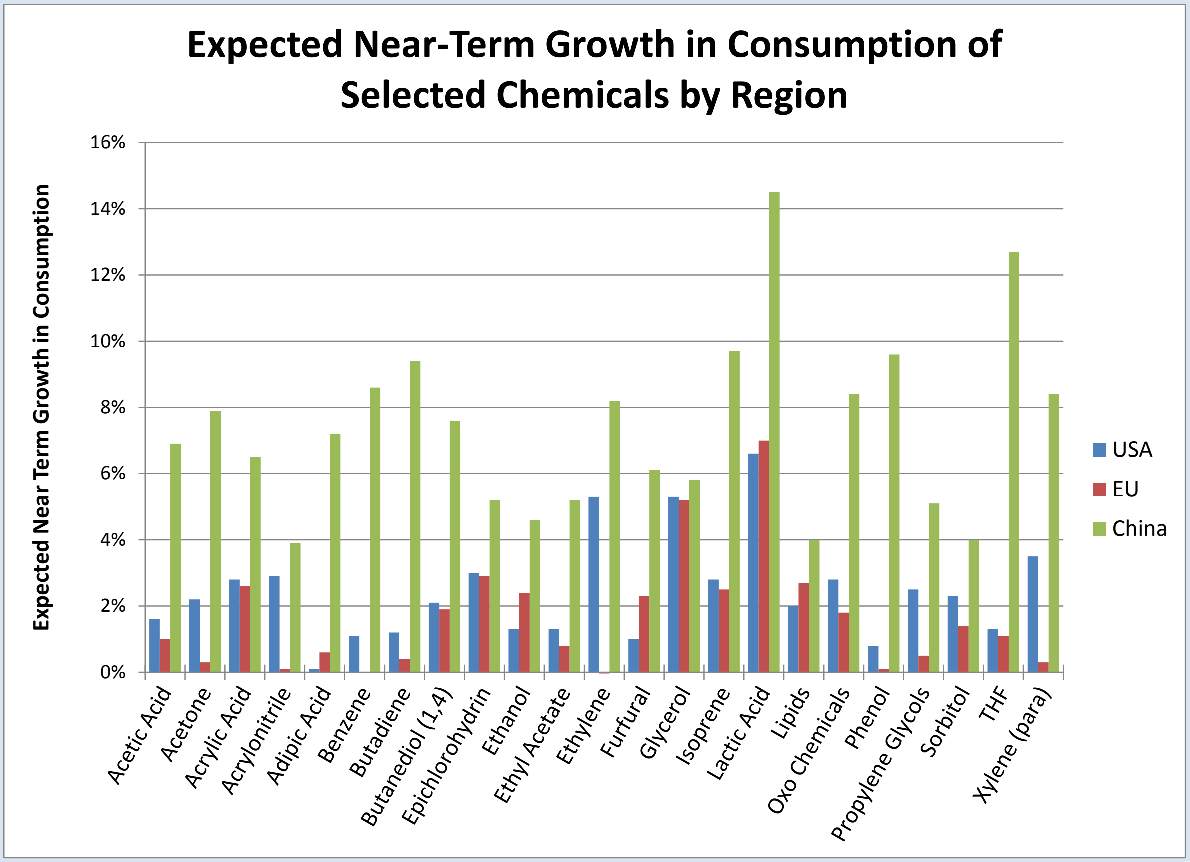

Figure 36. The near-term expected growth in consumption of chemicals follows the near-term expected GDP growth in the United States, European Union, and China[10]

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[10] Data reproduced and utilized with the permission of IHS Chemical.

Figure 37 is a Sankey diagram showing the production and consumption of selected chemicals in the United States, EU, China, and the rest of the world (IHS 2015a). Ethanol, ethylene, and lipids are the three largest chemicals on the global market. Note that most ethanol, especially in the United States, is blended into fuel. It was included in this chart to show the magnitude of ethanol production versus other commodity chemicals. The supply and demand varied widely by region. U.S. net exports were 4% of production, whereas the EU imported 11% net of its chemical supply. Consumption in China outpaced their domestic supply requiring that 23% (net) of its chemical demand was met by imports. Most of China's imports were met from regions outside the United States and the EU. Demand in Asia is expected to continue to grow suggesting that there is an opportunity for the United States to improve its trade balance by exporting bioproducts.

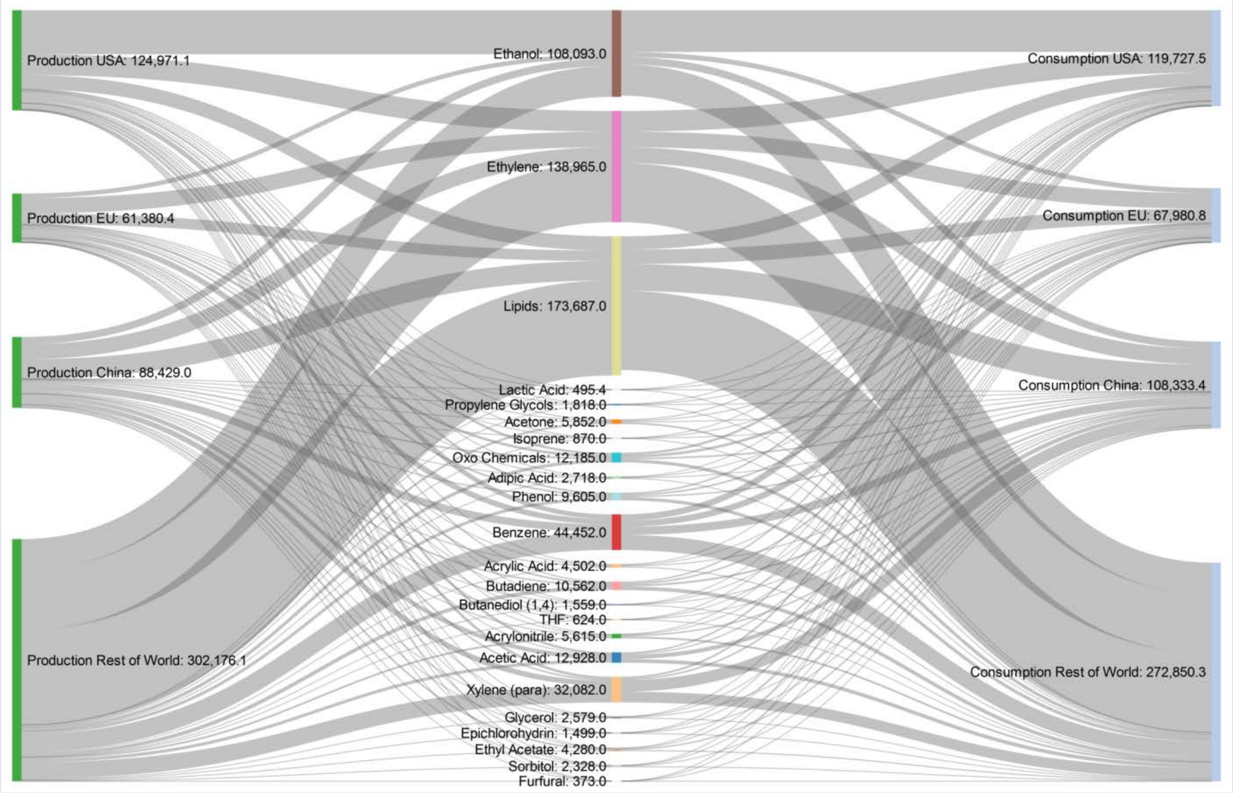

Figure 37. A Sankey diagram showing the production and consumption of selected chemicals by region—United States, European Union, China, and the rest of the world (IHS 2015a) (data from 2010-2014). All values are in metric tons per year.[11]

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[11] Data reproduced and utilized with the permission of IHS Chemical.

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