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Synthesis of ethylene glycol and terephthalic acid from biomass for producing PET

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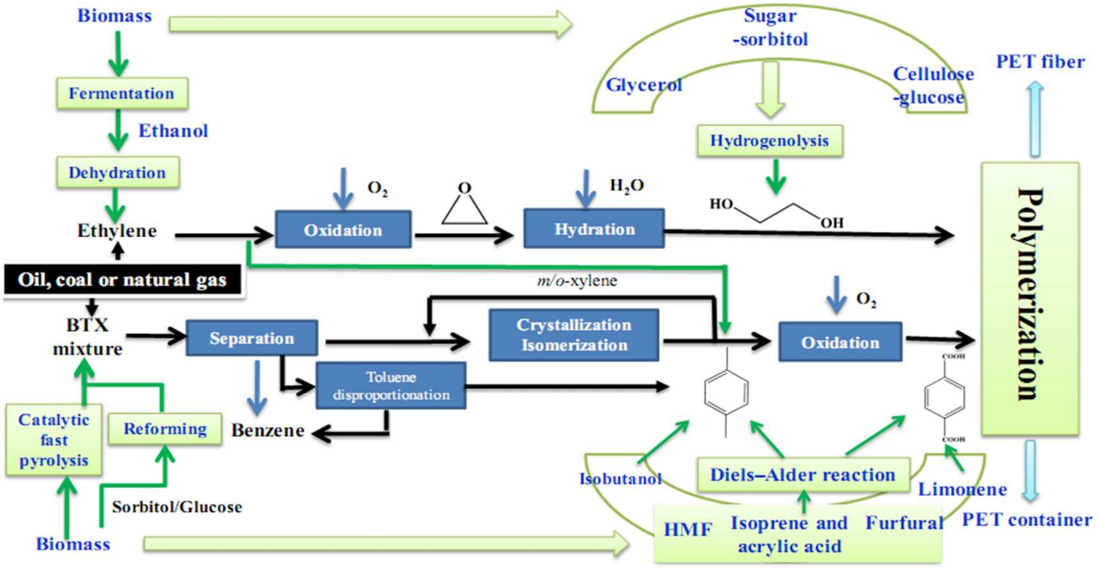
There have been considerable efforts to produce renewable polymers from biomass. Poly(ethylene terephthalate) (PET) is one of the most versatile bulk material used in our daily life. Recent advances in new catalytic process for conversion of biomass are allowing us to design more technically effective and cheaper methods for synthesis of green PET monomers. This review analyses recent advances in synthesis of PET monomers from biomass. Different routes for ethylene glycol (EG) and purified terephthalic acid (PTA) synthesis are systematically summarized. The advantages and drawbacks of each route are discussed in terms of feedstock, reaction pathway, catalyst, economics evaluation and technology status, trying to provide some state-of-the-art information on green PET monomers synthesis. Finally, an outlook is presented to highlight the challenges, opportunities and on-going trends, which may serve as a guideline for designing novel synthetic routes of green polymers from fundamental science to practical use.

1. Introduction and scope of review

One of the most widely used polymer, Poly(ethylene terephthalate) (PET), was first synthesized in 1941 by Whinfield J.R. and Dickson J.T. during a study of phthalic acid.[1] About ten years later, DuPont independently developed the low degree polymerized PET which has been produced at the industrial level since that time.[2] The consumption of PET is estimated to 100 million tons in 2016 and is currently growing at a rate of 4% per year.[3, 4] PET has the following properties: light in weight with high strength, low permeability of CO_2, and good light transmittance. More importantly, it does not have any negative health effects and is approved as a food and beverage container by government health organizations worldwide. PET is sold as either fibers (*ca.* 64% market), containers or packaging films.

PET is a kind of saturated polyester with average molecular weight of $2\text{-}5\times10^4$ depending on its applications. It is produced from monomers of ethylene glycol (EG, also named MEG in industry) and purified terephthalic acid (PTA) or dimethyl terephthalate (DMT). This polymerization process begins with the esterification or transesterification of monomers, and ends with further condensation to produce highly polymerized PET at reaction conditions of 533 K under vacuum of *ca.* 50 Pa.[4]

Commercially, EG and PTA or DMT are produced from ethylene and *para*-xylene (*p*-xylene), respectively. As shown in Scheme 1, currently in the dominant route for PET synthesis, ethylene is catalytically converted to ethylene oxide over silver catalysts,[5, 6] then the ethylene oxide is hydrated to EG either by noncatalytic or catalytic method.[7-10] *P*-xylene is obtained from separating BTX (Benzene, Toluene, Xylene) mixtures by a crystallization method. To maximize the *p*-xylene yield, isomerization and disproportionation technologies are employed for BTX conversion.[11-13] The *p*-xylene is further oxidized and purified to get the PTA for polymerization.[14-16] The prevailing ethylene and *p*-xylene are derived from non-renewable fossil-based feedstocks, i.e., oil, coal and natural gas. Due to the high pressure of greenhouse gas emission and fossil fuels depletion, the production of PET monomers from renewable resources such as biomass has gained significant attentions.



Scheme 1 Drop-in replacement of fossil based PET monomers from biomass

Biomass is defined as material of biological origin excluding material embedded in geologic formation and fossilized, which exist in different forms such as lignocellulosic biomass, edible biomass such as starch, sugars and non-sugar biomass such as bio-oil and algae.[17] Among biomass materials, the sugar based biomass is regarded as promising feedstock or intermediate for synthesis of chemicals and fuels.[18, 19] Nevertheless, the accessibility of sugars is different and highly dependent on its original structure in biomass. Lignocellulosic biomass is the most abundant terrestrial biomass, whose production is estimated to *ca*. 2×10^{11} T per year.[20] It is mainly composed of hemicellulose and cellulose, which are polysaccharides consisting of basic units of pentose and hexose, respectively.[21] The polysaccharides are surrounded by lignin, and rather recalcitrant to be degraded. Hence, many strategies have been dedicated to releasing sugars, such as diluted acid hydrolysis, enzymatic hydrolysis and alkaline hydrolysis, which show promising results for industrial applications.[22-25] In addition, sugars can be readily obtained from sugar plants or from hydrolysis of edible starch.[26]

Biomass has been selectively converted into various chemicals, fuels and materials.[27, 28] Some small molecular compounds retain the specific structures of biomass, which are difficult to be synthesized from fossil resources and deemed to be value-added. For instance, vanillin was synthesized from lignin through electro oxidation or enzymatic conversion. The obtained vanillin could be used for synthesis of chemicals and polymers due to its multi-functional groups, which could increase the value of lignin-based products and promote the economy of cellulosic biomass utilization.[29-32]

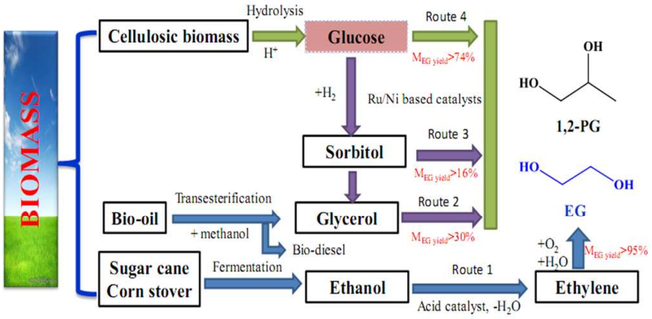
Some of chemicals derived from biomass are suitable to be used as monomers due to its unique structures and functional groups. A number of publications and reviews have been dedicated to the synthesis of green monomers from biomass.[33-38] For example, Lee et al. reviewed the production of monomers and possible polymers by enzymatic approaches.[35] Rose and Palkovits highlighted the recent achievements and potential routes for bio-based polymers from cellulosic biomass by using both bio and catalytic methods.[36] Mülhaupt reviewed the bio-based polymers from the economic and environmental points of view and listed the potential monomers derived from biomass.[37] Fenouillot et al. focused on the special polymers derived from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide).[34] Several potential routes to synthesize PET monomers from biomass have been proposed. These routes use both drop-in replacement of PET monomers or substitute for PET monomers with new types of monomers including 1,3-propanediol, isosorbide, 2,5-furandicarboxylic acid and 2,5-bis(hydroxymethyl)furan.[39, 40] These monomers could partially or totally substitute the monomers of EG or PTA for polyesters synthesis. However, there are some challenges in developing polymer substitutes for PET. For instance, the mechanical strength of poly (ethylene 2,5-furandicarboxylate) (PEF) is much lower than PET due to the lack of aromatic ring in PEF.[41] In addition, these new materials need approval from government agencies if they are to be used in the food and beverage packing industry. Some companies such as Coca-Cola have made great efforts to produce 100% renewable PET. These incentives greatly promoted the drop-in replacements of PET precursors from biomass.

This review attempts to exclusively focus on the synthesis of PET monomers via catalytic routes from biomass (Scheme 1). Four routes for EG synthesis and seven routes for PTA synthesis from biomass were summarized and discussed. The advantages and drawbacks of each route are addressed along with the discussion on challenges and opportunities.

2. Synthesis of EG from biomass

EG is the simplest diol molecule. In 2014, the global demand for EG reached 25 million tons with an estimated increase of 5%

each year. Globally, more than 58% of EG is used as a monomer to prepare PET. At present, the ethylene is obtained either from steam cracking of ethane (a by-product in fluid catalytic cracking in petroleum refinery), the catalytic cracking of petroleum, or from methanol by methanol to olefins process.[42-44]



Scheme 2 Four routes for EG synthesis from biomass.

In the past decade, there has been an increasing demand to try and produce EG from biomass.[45-47] For example, Yue et al. highlighted the EG properties, synthesis, and applications from the viewpoint of catalysts and reaction mechanisms. They focused on the properties or industrial production of EG from fossil energy and biomass. [47]

Up to now, EG can be synthesised from biomass using four different feedstocks: ethanol, glycerol, sorbitol, sugars and cellulosic biomass. These processes and intermediates of reactions are listed in Scheme 2.

2.1 Synthesis of EG from ethanol

Ethanol is one of the most versatile platform chemicals and fuel additives. It is widely used as feedstock for synthesis of *n*-butanol, butadiene and acetaldehyde.[48-51] The global production of ethanol reached 70 billion liters in 2010, and this number is expect to 113 billion liters in 2017.[50]

Due to the abundant supply of bio-ethanol in some areas and the market demand for renewable EG, the synthesis of green EG with ethanol as a feedstock has been realized at a commercial level. The route using ethanol for EG synthesis involves three major steps: 1) dehydration of ethanol to ethylene; 2) oxidation of ethylene to ethylene oxide; 3) hydration of ethylene oxide to EG.

The main obstacle of this route is the high cost of ethanol feedstock compared to fossil ethylene.[52, 53] In detail, the cost of sugarcane bio-ethylene production is relatively low in Brazil and India, which is around \$1200 (including all costs, all prices in this review are reported in US dollars) per ton. However, the bio-ethylene derived from sweet sorghum in China is estimated to \$1700 per ton, and this number increases to \$1900-2000 per ton for lignocellulosic biomass ethanol derived ethylene**.** In contrast, the cost of petrochemical ethylene is dependent on the region with a global average cost of *ca.* \$1100 per ton in recent years.[54]

The pioneer of this route is JBF Industries Ltd., who produces bio-EG for Coca-Cola. The plant is located in southern Brazil, which has unique resource of dense sugarcane plantation. The capacity of renewable EG they produced was 500 kT per year, which is equivalent of more than 1.5 million barrels of oil.[55, 56] Due to the large market of EG in Asia area, a new bio-EG plant was built in Taiwan in 2013 by Greencol Taiwan Corporation (GTC). The feedstock is sugarcane derived ethanol, which is provided by Petrobras from Brazil.[57, 58]

2.2 Synthesis of EG via hydrogenolysis of glycerol

Since the end of 20th century, the decline of fossil oil reserves and environmental issues stimulated the rapid development of biodiesel industry. As the co-product of biodiesel, the production of glycerol increased dramatically from 750 kT in 2008 to 2 million T in 2015.[59-61] Glycerol can be used as a feedstock to produce a wide range of commodity chemicals including dihydroxyacetone, 1,2-propylene glycol (1,2-PG), 1,3-propylene glycol (1,3-PG), acrolein and hydrogen.[62-67]

Besides primary product of 1,2-PG, hydrogenolysis of glycerol also produces EG, methane, methanol and COx as co-products. The diols selectivity could be turned by using different catalysts. Over Pt, Pd and CuO catalysts, the main product was 1,2-PG with negligible EG formation.[68-71] In contrast, the selectivity of EG was much higher with Ru and Ni as catalysts, as shown in Table 1. Miyazawa et al. investigated the conversion of glycerol with noble metal and acid catalysts.[72] They found that Ru/C catalysts produced 3-5 times higher selectivity than other noble metals and acid catalyst under concentrated feedstock (20 wt%).[73] Nickel catalysts are also very active for C-C cleavage. Yin et al. employed Raney Ni as a catalyst for producing glycols, and obtained 56.3% selectivity of EG at 41.1% glycerol conversion.[74] Tomishige's group investigated the bimetallic catalyst of PtNi and obtained 48% EG selectivity and 16% glycerol conversion.[75] The additives and supports were found to affect the chemical and physical states of Ni, and consequently changed the diols selectivity. Yu et al. modified Ni catalysts with different metal including Sn, Ce, Co, Cu, Al and Fe. The best result was found over Ce modified Ni catalysts, which afforded 90.4% glycerol conversion with more than 60% 1,2-PG and 10.7% EG selectivity.[76] Ryneveld et al. studied Ni catalysts for glycerol conversion under different conditions, and found that high hydrogen pressure favoured the EG formation.[77]

Table 1 Catalytic conversion of glycerol to EG over Ru and Ni based catalysts[a]

Catalyst	Reaction conditions	$C_{Glycerol}$ /%	Con. /%	EG sel. /%	Ref.
Ru/C	393 K, 8 MPa H_2 for 10 h	2	20.8	7.6	72
Ru/C	393 K, 8 MPa H_2 for 10 h	20	14.9	40.2	
Ru/SiO_2	493 K, 5 MPa H_2 for 10 h	60	24.3	25.7	73
Raney Ni	453 K, 0.1 MPa N_2 for 1 h	10	41.1	56.3	74

Ni-Ce/AC	473 K, 5 MPa H_2 for 6 h	25	90.4	10.7	76
Ni/SiO_2	503 K, 6 MPa H_2	60	16.2	13.5	77
PtNi/Al_2O_3	453 K, 8 MPa N_2 for 24 h	5	16	48	75
PtNi/Al_2O_3^{b}	453 K, 8 MPa N_2 for 24 h	5	64	42	
PtNi/Al_2O_3 ^{b}	453 K, 8 MPa N_2 for 72 h	5	83	36	

[a] Reactions were conducted in a batch reactor except for Ni/SiO_2 catalyst; other products in this reaction include 1,2-PG, propanol, ethanol, methanol and methane. $C_{Glycerol}$, Con. and sel. represent concentration of glycerol, conversion and selectivity, respectively. [b] Catalysts amount was increased from 0.2 g to 1.0 g.

Most researchers are trying to produce 1,2-PG and 1,3-PG rather than EG due to the higher economic potential and value of PG.[78] Moreover, the insufficient supply of glycerol, poor EG selectivity and difficulty in controlling C-C and C–OH cleavage limit this route for focusing on EG synthesis.

2.3 Synthesis of EG via hydrogenolysis of sorbitol and xylitol

A DOE (US Department of Energy) report identified sorbitol as one of the 12 important platform chemicals derived from biomass for producing fuels and chemicals.[79-82] Sorbitol is produced from the hydrogenation of glucose over Ni or Ru catalysts. Recently, research efforts have been made to develop technology for conversion of non-edible cellulose and lignocellulosic biomass into sorbitol by coupling the cellulose hydrolysis and sugar hydrogenation reactions in one-pot.[83-86]

Among various methods for sorbitol conversion, catalytically transforming sorbitol to glycols is a promising way due to its advantages of high atom economy and relatively mild reaction conditions. To get a high yield of low carbon glycols, the reaction for cleavage of C-C and C-OH bonds should be balanced. The primary catalysts used for this reaction are metallic Cu, Ni and Ru catalysts, which are summarized in Table 2.

The first report on sorbitol hydrogenolysis was present in 1933 by Zartman et al., who investigated the conversion of sugars over Cu/Cr_2O_3 catalysts under 30 MPa hydrogen at 523 K.[87] Afterward, Ni based catalysts attracted great interests due to their high activities. Clark used diatomite supported Ni catalysts in the presence of an alkaline additive for this reaction at different temperatures and hydrogen pressures.[88] The yields of glycerol and EG were 40% and 16%, respectively, at 488 K under 14 MPa hydrogen pressure. Tanikella used Ni/SiO_2-Al_2O_3 catalysts in methanol or ethanol solvent for hydrogenolysis of polyols to EG and 1,2-PG. With the addition of alkali, the EG yield reached 25%, which was similar to the yield of 1,2-PG.[89]

The promoter, alkaline and catalysts preparation methods remarkably affected the final glycol selectivity. For instance, Werpy et al. employed different Re modified catalysts for sugar alcohol conversion, and obtained superior selectivity to glycols. The yield of 1.2-PG and EG was 53.5% and 19.5%, respectively, over 5%Ni/5%Re, Eng 95 catalysts.[90] Liu et al. prepared skeletal Ni catalysts modified with different elements (ranging from groups 7 to 11 in periodic table of elements and B, P, Sn, In, Te, La, Ce). With the addition of Sn, the formation of organic acids were depressed and diols yield of 1,2-PG and EG reached 47.7%.[91] Ye et al. investigated the influence of catalyst preparation methods on sorbitol conversion. They found that the catalysts prepared by co-precipitation method enhanced glycols yield to 60%, which had higher stability as compared to these catalysts prepared by deposition–precipitation method.[92] The catalyst support is another variable that affects the glycols yield. Banu et al. loaded Ni and Pt on NaY zeolite and obtained high yields of 1,2-PG and glycerol from sorbitol. The changes of glycols distribution may be attributed to the pore structure of zeolites. Density functional theory (DFT) study unveiled that the adsorption of sorbitol on the metal clusters on zeolites leads to elongation of the C–C bonds and contraction of the C–O bonds, which facilitates the cleavage of C-C bonds of sorbitol.[93, 94] To avoid the usage of alkaline promoter, Chen et al. loaded Ni particles on MgO for sorbitol conversion. The catalysts showed high selectivity to 1,2-PG and EG, which reached 33.7% and 26%, respectively. However, the catalysts were not very stable under hydrothermal conditions.[95]

Table 2 Catalytic conversion of hexitols into glycols[a]

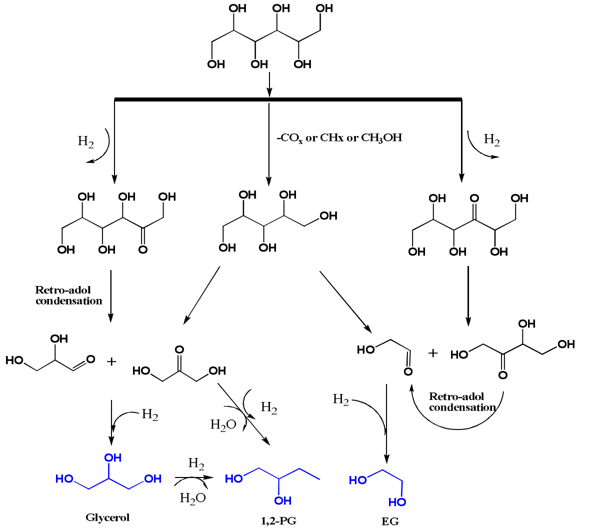
Catalyst	Reaction conditions	$C_{hexitol}$ /%	Con. /%	1,2-PG sel. /%	Glycerol sel. /%	EG sel. /%	Ref.
Ni/kieselguhr+Ca$(OH)_2$	488 K, 14 MPa H_2, 150 min	40	96	17	40	16	88
Ni/SiO_2–Al_2O_3	548 K, 27.6 MPa H_2, 1 h	35	--	27	--	25	89
Ni-Re/AC+KOH	493 K, 4.14 MPa H_2, 4 h	25	39.3	30	19	16	90
Ni or Ru	503 K,12 MPa H_2, 20-50 min	25	95	37.4	16.8	15.8	96
Ni-Sn alloy+NaOH	488 K, 10 MPa H_2, 6 h	25	89.1	35.0	--	12.7	91
Ce–Ni/Al_2O_3-CP	513 K, 8 MPa H_2, 7 h	30	91.1	35.3	10.3	17.9	92
Ni_2P/AC+Ba$(OH)_2$	473 K, 4 MPa H_2, 45 min	5	98.6	27.7	--	17.0	97
Ni/NaY	493 K, 6 MPa H_2, 6 h	15	68	60	15	7	93
Ni/NaY	493 K, 6 MPa H_2, 6 h	20	66	62	14	7	94
Ni/MgO	473 K, 4 MPa H_2, 4 h	20	67.8	33.7	21.1	26.0	95
sulfur-modified Ru/C+CaO	513 K, 17 MPa H_2, 7 h	33.3	98	64.6	3.1	26.2	98
Ru/CNF/GF_2-HCl+CaO	493 K, 8 MPa H_2, 6 h	20	35.8	40.8	14.7	23.6	99

Ru/CNF+CaO	493 K, 8 MPa H_2, 4 h	20	36.4	20.2	15.9	38.4	100

[a] $C_{hexitol}$, Con. and sel. represent concentration of hexitol, conversion and selectivity, respectively; all the reaction were conducted in a batch reactor; by-product in this reaction include 1,4-butanediol, lactic acid, ethanol, acetic acid, methanol and formic acid.

Various Ru catalysts in different states were also employed for sorbitol conversion. Dubeck et al. employed a sulfur-modified Ru catalyst for producing EG and 1,2-PG from sorbitol. The modification of Ru decreased the yield of glycerol, but enhnced the selectivity of 1,2-PG and EG to 64.6% and 26.2%, respectively.[98] Zhou et al. used carbon nano fiber supported Ru catalyst for sorbitol hydrogenolysis. Even though the catalysts showed moderate activity for 1,2-PG production, the EG yield was improved to 38.4%, which was attributed to the high dispersion of Ru and proper porosity of the carbon support .[99, 100]

The conversion of xylitol to glycols is very similar to the sorbitol hydrogenolysis. However, the products distribution is different. A higher yield of EG than 1,2-PG was obtained from xylitol in contrast to lower EG yield obtained in sorbitol conversion. As reported by Tanikella et al., the yield of EG and 1,2-PG reached 45% and 33%, respectively, over the catalyst of Ni/SiO_2-Al_2O_3 in a solvent of methanol or ethanol.[89] Sun et al. studied the conversion of xylitol with different noble metal catalysts in the presence of $Ca(OH)_2$. They found that the selectivity of diols is strongly dependent on the active sites of metals and their supports. Ru supported on active carbon exhibited superior activities, and EG yield surpassed 32% with 1,2-PG yield of 25%.[101] Huang et al. developed Cu/SiO_2 catalysts for xylitol conversion. The overall yield of EG and 1,2-PG reached 54.4% at nearly 100% xylitol conversion in the presence of $Ca(OH)_2$.[102]



Scheme 3 Conversion of sorbitol to glycols (modified from ref.[94, 103]).

As shown in Scheme 3, the conversion of sorbitol to low carbon glycols is a parallel reaction. The selectivity of glycols is determined by the cleavage of different C-C bonds over catalysts.[94, 103] Montassier et al. proposed that the mechanism for sorbitol hydrogenolysis involves dehydrogenation, retro-aldol condensation and retro-Michael reactions. The C-C bonds cleavage in sorbitol was attributed to the retro-Michael reactions.[104] Sun et al. investigated the xylitol conversion with different catalysts. They postulated that the C–C bonds cleavage was most likely via the base-catalyzed retro-aldol condensation based on the intermediates monitoring.[101]

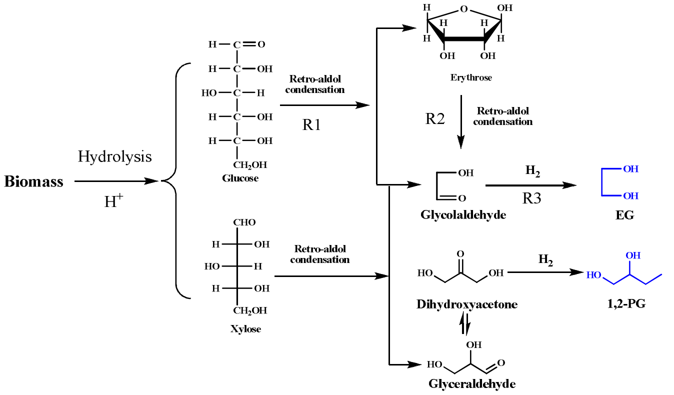
Even though the main products of sorbitol hydro-cracking is 1,2-PG, more than 10% EG will be produced during the reaction. Therefore, it could be regarded as another candidate method for the production of green EG. In 2008, hydrocracking of glucose-sorbitol to 1,2-PG and EG was operated at a commercial scale of 200 kT per year in Changchun Dacheng Industrial Group Company Ltd.. In addition, with the rapid development of hemicellulose extraction and conversion, xylose or xylitol could represent a potential starting material for synthesis of EG due to its high EG selectivity.[105, 106]

2.4 Synthesis of EG via cellulosic biomass conversion

It is highly desirable to produce fuels and chemicals from cellulosic biomass, the most abundant components in lignocellulosic biomass.[107-109] Nevertheless, cellulose is very reluctant to be degraded due to its high crystallinity and dissolution properties in most solvents, and its selective conversion is still a challenge.[110-114]

Direct conversion of lignocellulose to EG (DLEG) is a newly emerged route for the synthesis of EG. In 2008, Ji et al. first employed a tungsten carbide catalyst, whose electronic properties are similar to that of Pt-group metals,[115] for cellulose conversion.[116-118] Very differing from the catalytic performance of noble metals, the main product over tungsten carbide catalysts was EG, which reached 27% yield at 98% cellulose conversion. Doping the tungsten carbide catalyst with Ni increased the EG yield up to 61% with total cellulose conversion. To improve the dispersion of tungsten carbide, Zhang et al. prepared a mesoporous carbon support which had three-dimensional pores. Compared with conventional activated carbon possessing microporous structures, the mesoporous carbon supported tungsten carbide catalyst exhibited higher selectivity towards EG (72.9% yield).[119] Zheng et al. prepared a series of M(8,9,10)-W bimetallic catalysts on different supports for cellulose conversion. The EG yield reached 76.1% over Ni-W/SBA-15 catalysts. Meanwhile, the authors also found that polyols yield could be tuned by changing the ratio of transition metals and metallic tungsten which took charge of hydrogenation and C-C cleavage reactions, respectively.[120] Zhao et al. studied the performance of tungsten phosphide in this reaction. Very similar to the performance of tungsten carbide, the EG yield was maximized with the doping of Ni to tungsten phosphide.[121] The support of catalysts also affects the EG yield. For instance, Baek et al. loaded the NiW particles on SiO_2-Al_2O_3 for cellulose conversion, and obtained a glycols yield of less than 40%.[122, 123] Some amount of tungsten species (*ca.* 100 ppm in reactant solution) was detected in the liquid solution after reaction demonstrating that this catalyst could not be stable for long term operation. On the basis of characterizing the spent catalysts and in-depth understanding the reaction mechanisms, a series of binary catalysts (Ru, Ni based metallic catalysts + W based catalyst) were developed for the synthesis of EG.[124-126] Tai et al. employed binary catalysts of Ru/AC-tungstic acid for cellulose conversion, and obtained 50% EG yield. Thanks to the temperature controlled-phase-transfer properties of tungstic acid and good hydrothermal stability of Ru/AC, the catalyst could be reused for 20-30 times.[124] In another study, Liu et al. combined the Ru/AC with WO_3 for controllable synthesis of 1,2-PG and EG. By designing the WO_3 structure, the competitive reactions of the sugar hydrogenation and degradation were adjusted, and the selectivity of 1,2-PG and EG was improved to 40.9% and 22.7%, respectively, with 21.2% cellulose conversion over $50\%WO_3/Al_2O_3$ + C_{act} catalysts.[125] Afterwards, cheaper and robust binary catalysts of Raney Ni and tungstic acid were developed, which gave 10% higher yield of EG than Ru/AC-tungstic acid catalysts.[126] The superior performance of the Raney Ni-tungstic acid catalyst makes it be of great potential to be used in a large scale conversion of cellulosic biomass.

Motivated by the application of DLEG process, different kinds of lignocellulosic biomass including corn stalk, poplar wood, *Miscanthus* were used as feedstocks for EG synthesis.[127-132] Pang et al. found that the lignin in the corn stalk inhibited the cellulosic biomass conversion and decreased the EG yield. After successive pretreatments of ammonia and H_2O_2, both cellulose and hemicellulose in corn stalk were effectively converted to EG and 1,2-PG with an overall yield of 48% (the carbon yield based on whole feedstock).[127] For woody biomass such as poplar wood, the carbohydrate components of cellulose and hemicellulose were converted to EG and 1,2-PG, and partial lignin component can be degraded to phenols even without any pretreatment.[128] The different reaction results between grassy biomass and woody biomass may be attributed to the original difference in the feedstock structures. Fabičovicová et al. investigated the conversion of cellulose and woody biomass over Ru/W/AC catalysts, the EG yield was about 30% at 5% feedstock concentration at 493 K for 3 hours.[132] To further improve the reaction efficiency, Pang et al. studied concentrated feedstock conversion for EG synthesis. After removing the lignin and surface protectors from the *Miscanthus*, 39% EG yield was obtained under 10% feedstock concentration, the reaction pathway is shown in Scheme 4. In a subsequent work, they investigated the effect of biomass-contained inorganic impurities on cellulose conversion and EG yield.[133] Recently, partial green PET was synthesized from green EG, which showed comparable properties to fossil PET when the impurities of glycols was below 5%.[4]



Scheme 4 The reaction pathway for conversion of cellulose and hemicellulose to EG. (modified from ref. [131])

The reaction mechanism of the DLEG process involves cascade reactions, including cellulose hydrolysis, retro-aldol condensation and hydrogenation reactions.[134-136] As shown in Scheme 4, cellulose is hydrolyzed to sugars by acids arising from catalysts (such as tungstic acid) and subcritical water. The C-C bonds are then selectively cleaved by tungsten species through a retro-aldol condensation pathway. Finally, the EG precursor, glycolaldehyde, is hydrogenated to EG by hydrogenation catalysts such as Ru and Ni catalysts. In hot water and H_2 atmosphere, the tungstic acid was transformed to soluble H_xWO_3, which was deemed as genuine active species for the catalytic retro-aldol condensation of sugars.[134]

According to the reaction mechanism, sugars are important intermediates for cellulose conversion, and suitable to be used as candidate feedstocks for EG synthesis.[137, 138] Zhao et al. converted concentrated glucose (10-50 wt%) to EG at a yield of 60% with a binary catalyst of ammonium metatungstate (AMT) and Ru/AC. The reaction kinetics study disclosed that pseudo-first order reaction of glycolaldehyde formation *vs.* pseudo-second order reaction of side reactions of glycolaldehyde account for the sensitivity of EG formation. The big discrepancy in activation energies (141-148 kJ/mol vs. 38-49 kJ/mol) between glucose hydrogenation and retro-aldol condensation of glucose leads to the dependence of product distribution on the reaction temperature.[139-141] In addition, the presence of tungstate species significantly retarded the rate of aldoses hydrogenation over the Ru catalyst due to the competitive adsorption of aldoses and tungstate species, which facilitated the C-C bonds cleavage of aldoses and consequently increased the EG yield.[140-142] Ooms et al. also investigated the conversion of glucose to EG over a tungsten carbide catalyst in a semi-continuous autoclave, and obtained an optimal EG yield up to 66%.[138]

Besides tungstic catalysts, many progresses in catalyst design have been achieved for conversion of cellulose to glycols.[143-150] For example, Wang et al. prepared a series of Ni-based catalysts on different supports, and found that Ni loaded on ZnO favoured the formation of 1,2-PG and EG with yield of 34.4% and 19.1%, respectively.[143] Xiao et al. prepared a CuCr catalyst for the conversion of concentrated cellulose and glucose.[147] The total glycols yield reached 68.7% with 30.8% EG yield in the presence of $Ca(OH)_2$. Sun et al. developed a binary nickel-lanthanum(III) catalyst for cellulose conversion, over which the overall yield of EG and 1,2-PG reached 63.7%. Moreover, the concentration of lanthanum oxide could be as low as 0.2 mmol/L without notable loss in glycols yield. Based on DFT calculations and experimental analysis, a dual routes mechanism was proposed, wherein the major route is selectively cracking sugars into C2 molecules, and the minor route is hydrogenolysis of sugar alcohols.[148] Xi et al. used a Ru/$NbOPO_4$ catalyst for cellulose conversion, and obtained 54.5% total yield of EG and EG monoether at 493 K in methanol solvent. Effects of dopants (W, Sn, Ni, Cu) on EG yield were investigated, and the overall yield of EG and EG monoether was enhanced to 64% with the promotion of Ni.[149] Li et al. synthesized a series of Pt/CNT(carbon nano tube) catalysts for cellulose conversion, the total yield of EG and 1,2-PG reached 71.4% .[150]

By enormous endeavours of researchers, varieties of catalysts were developed for conversion of cellulose to EG. The EG selectivity was promoted to *ca.* 75%, and the feedstock was extended from microcrystalline cellulose to concentrated glucose and lignocellulosic raw biomass (up to 10 wt%). Based on the consideration of feedstock availability and EG selectivity, the sugar-sorbitol and DLEG processes were regarded as promising routes for EG synthesis.

2.5 Comparison of different biomass-based routes for EG synthesis

Four routes have been developed for EG synthesis from biomass, and each of them has specific advantages and disadvantages. As shown in Table 3, the yield of EG from ethanol is as high as 90%. However, the prevailing ethanol is derived from sugars with elevating cost, and the fermentation of ethanol from lignocellulosic biomass is still under development. Even though the yields of EG from glycerol and sorbitol are less than 30%, some valuable products such as 1,2-PG will be produced, which may improve the overall economic evaluation. One-pot conversion of cellulose to EG is very attractive due to the high selectivity. However, cellulosic reactant is solid and cannot be pumped to reactor continuously. The reaction efficiency is yet to be improved. Among these four approaches, the catalysts of ethanol route have been commercialized. Other routes of glycerol, sorbitol and cellulose conversion are conducted in hydrothermal conditions, which requires the development of more hydrothermal-tolerant catalysts.

In addition, in these routes for green EG synthesis, certain non-biomass chemicals are introduced into the final products during its multi-step reactions. For instance, hydrogen is indispensable reagent for hydrogenolysis of glycerol, sugar, sorbitol and cellulose, which is derived from fossil energy. However, it will be gradually replaced by green hydrogen with the rapid development of biomass reforming and electricity generated from wind and solar energy.[151]

Recently, some new strategies have been proposed to synthesis EG from renewable energy, such as solar energy. Liquid Light Corporation employed carbon dioxide and light for EG synthesis, which harnesses CO_2 economically with bio-EG.[152] In 2015, Liquid Light and Coca-Cola were cooperated to accelerate the development of this technology for green EG synthesis.[153]

Table 3 Analysis of different routes to produce green EG

Feedstock	EG yield /%	Advantages	Disadvantages
Ethanol	>90[a]	High selectivity	High cost of ethanol
Glycerol, glucose, sorbitol	25-29[a]	Produce value added coproducts	Limited feedstock, catalysts activity
Cellulose[b], glucose	75	High selectivity	Low reaction efficiency[b]

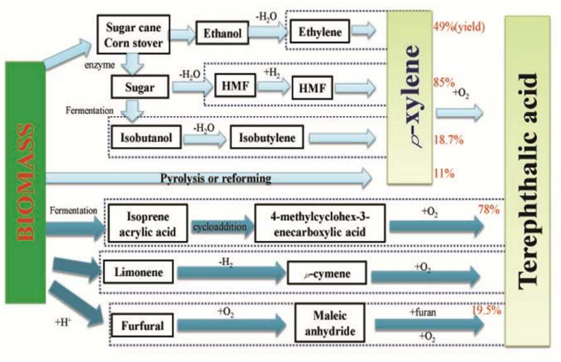
[a] the yield was calculated based on the maximized mass yield of each reaction step ever reported; [b] the cellulose conversion was conducted in batch reactors with low concentration of feedstock.

3. Synthesis of PTA from biomass

Another monomer for PET manufacture is purified terephthalic acid (PTA). The global production of PTA reached 57 million tons in 2014 with 6% annual increase in the past several years.[154, 155] Currently, terephthalic acid is produced via catalytic aerobic oxidation of *p*-xylene with air in acetic acid medium, which is known as the AMOCO process. The 4-carboxybenzaldehyde impurity in crude terephthalic acid must be reduced to levels less than 25 ppm to obtain the polymer grade PTA.[156, 157]

The industrial *p*-xylene is derived from the catalytically reformed naphtha and pyrolysis distillates, as shown in Scheme 1.[158, 159] In the past decade, seven routes have been studied for bio-based *p*-xylene or PTA synthesis:

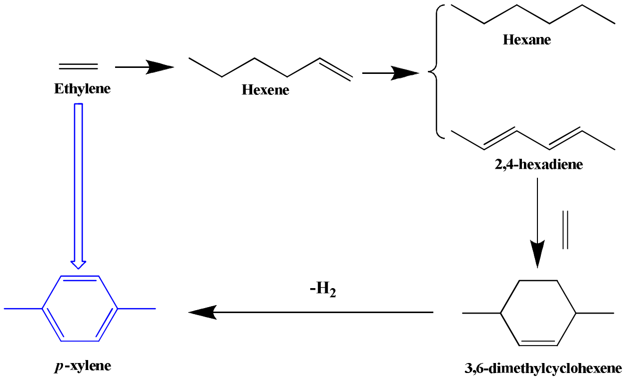
Synthesis of *p*-xylene from 1) bio-ethylene, 2) 5-hydroxymethylfurfural (HMF), 3) isobutanol and 4) pyrolysis or reforming; synthesis of PTA from 5) isoprene and acrylic acid, 6). limonene and 7) furfural. The processes, react intermediates and typical yields are listed in Scheme 5.



Scheme 5 Different routes for terephthalic acid synthesis from biomass

3.1 Synthesis of *p*-xylene from bio-ethylene

The conversion of ethylene to *p*-xylene is a complicate multi-step reaction, which include trimerization of ethylene to hexene, catalytic disproportionation of hexene to 2,4-hexadiene, Diels-Alder reaction between ethylene and 2,4-hexadiene, and dehydrogenation of 3,6-dimethylcyclohexene to *p*-xylene, as depicted in Scheme 6.



Scheme 6 Synthesis of *p*-xylene from ethylene (modified from ref.[160])

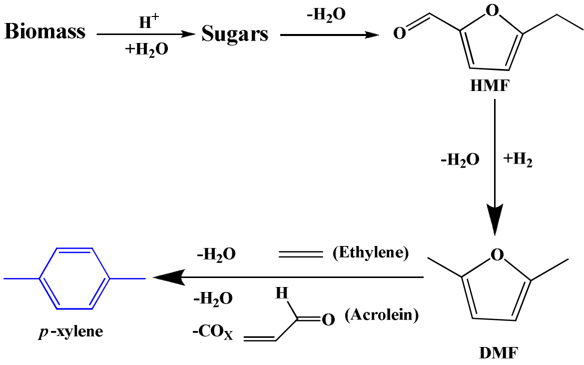
Because hexene is a useful co-monomer for the production of linear low density polyethylene (LLDPE), trimerzation of ethylene to hexene has been widely investigated.[161-165] In a typical commercial process, the selectivity of hexane surpassed 90% over catalysts of chromium complexes. The main obstacle for *p*-xylene synthesis following this route is the catalytic disproportionation of hexene to 2,4-hexadiene, which generally has poor selectivity to final product. Recently, Lyons et al. employed an Ir complex catalyst for the hexene disproportionation, and obtained a TON of 777 under 453 K for 3.5 hours. Subsequently, the authors synthesized 3,6-dimethylcyclohexene from the products of hexene disproportionation via Diels-Alder reaction. Both 2,4-hexadiene and 1,3-hexadiene were converted to 3,6-dimethylcyclohexene with 23.9% selectivity at 523 K for 48 h under 4.1 MPa of ethylene. The authors also tried the one-pot conversion of hexene and ethylene to 3,6-dimethylcyclohexene. The selectivity of 3,6-dimethylcyclohexene reached 65.5% upon enough reaction time (192 h). Finally, 3,6-dimethylcyclohexene was dehydrogenated to *p*-xylene with commercial catalysts of Pd/C, Pt/C, and Pt/Al_2O_3.[160]

This newly emerged process employed sole feedstock of ethylene, which could be obtained from bio-ethanol.[166] For some special area such as Brazil, the continuous supplement of cheap bio-ethylene could promote this process for commercialization. However, the intermediates in this reaction are not very stable. Side reactions concurrently happen, which poison the catalysts and decrease the final *p*-xylene yield. More efforts should be made on improving the reaction efficiency and replacing the homogeneous catalysts.

3.2 Synthesis of *p*-xylene from HMF

As one of the top ten value-added bio-based chemical defined by DOE, HMF has attracted great attentions.[167] Recently, significant advances have been achieved for the production and utilization of HMF. A number of publications including some excellent reviews have been dedicated to this topic.[168-172] For instance, Dutta et al. reviewed the transformation of biomass to HMF with different feedstocks and catalysts.[168] They also summarized the applications of HMF, especially in polyesters and fuels.[173] Teong et al. reviewed the development timeline of HMF during the past 130 years.[171] More importantly, the pilot plant of HMF has been demonstrated by AVA Biochem company in Switzerland at a scale of 20 T per year in 2014.[174]

Conversion of biomass to *p*-xylene with HMF as an intermediate is outlined in Scheme 7. Biomass is hydrolyzed to sugars and then dehydrated to HMF, which is further hydrodeoxygenated to 2,5-dimethylfuran (DMF). Finally, DMF reacts with ethylene or acrolein via Diels–Alder reaction to form *p*-xylene with the removal of water or COx.



Scheme 7 Synthesis of *p*-xylene from HMF.

Among these successive reactions, selective conversion of HMF to DMF attracts significant attentions because of the superior properties of DMF.[175, 176] There are three different functional groups in HMF, including an aldehyde group, a hydroxyl group, and a furan ring. Various side reactions might occur under reaction conditions. It is crucial to select an appropriate solvent and catalyst for the conversion of HMF to DMF.[175] In 2007, Román-Leshkov et al. developed a biphasic system for catalytic conversion of sugars to DMF. Fructose was dehydrated to HMF by acid catalysts, and then extracted to the organic phase for hydrogenation with a CuRu/C catalyst. The biphasic system effectively removed the products and promoted the conversion of HMF. As a result, the DMF yield increased to 79% after 10 hours reaction at 493 K.[177] After that, different solvent systems were disclosed for the synthesis of DMF from biomass. Binder et al. reported the conversion of raw biomass to DMF in N,N-dimethylacetamide (DMA)-lithium chloride (LiCl) solvent.[178] The DMF yield was 49% in the presence of CuRu/C catalysts. However, the yield decreased to 9% with untreated corn stalk as a feedstock. Chidambaram et al. employed ionic liquid as a solvent for the synthesis of DMF. With the addition of acetonitrile, DMF yield reached 32% with Pd/C as a catalyst.[179] Thananatthanachon et al. explored a versatile solvent, formic acid, which promoted the dehydration of fructose and the hydrogenation of HMF. The DMF yield reached 95% over Pd/C catalysts.[180] Recently, numerous studies have been done on the development of novel catalysts,[181-185] hydrogen resource,[186] solvent[187] and reaction mechanisms[188, 189] for this reaction, which promoted the synthesis and utilization of DMF.

Both ethylene and acrolein could react with DMF to produce *p*-xylene through Diels–Alder cycloaddition reaction. Brandvold et al. at UOP first developed the route for *p*-xylene synthesis with HMF and ethylene, and obtained 30% theoretical yield.[190] Then, Williams et al. reported the cycloaddition of ethylene and DMF to synthesis *p*-xylene by using HY zeolite catalysts. The *p*-xylene selectivity was as high as 75% with *n*-heptane as a solvent at 573 K.[191] Do et al. employed advanced separation and analytical techniques, including extensive 1D and 2D NMR, to elucidate the reaction network of Diels−Alder over catalysts of HY zeolite.[192] Chang et al. investigated different catalysts for this reaction, and the yield of *p*-xylene was improved to 90% over H-BEA catalysts.[193] Afterwards, the same group employed molecular simulation to unveil the effect of solvent on this reaction. The results indicated that the presence of *n*-heptane reduced side reactions, enhanced hydrophobic environment in the zeolite, and then improved the *p*-xylene selectivity.[194] The DFT study of reaction between ethylene and DMF was analyzed by Nikbin et al. The results of DFT calculations on electronic structure showed that the DMF-ethylene cycloaddition is thermally feasible, and the kinetic limitation of the Diels–Alder and dehydration reactions are dependent on the Lewis acids or Brønsted acids in catalysts.[195] The economic analysis of *p*-xylene production from HMF by Lin et al. showed that the minimum *p*-xylene cost is estimated to be $3962/metric ton, and the dominant cost is the HMF cost. [196]

Another attractive reactant for Diels–Alder cycloaddition with DMF is acrolein, which can be produced from glycerol via dehydration.[197, 198] Shiramizu et al. studied the kinetic and thermodynamic data for the Diels–Alder reaction of DMF with acrolein and obtained a 34% *p*-xylene yield at 213 K.[199] Even though the reaction temperature and catalysts of this approach are not very practicable, this process still gave us valuable insight into how *p*-xylene could be produced from biomass.

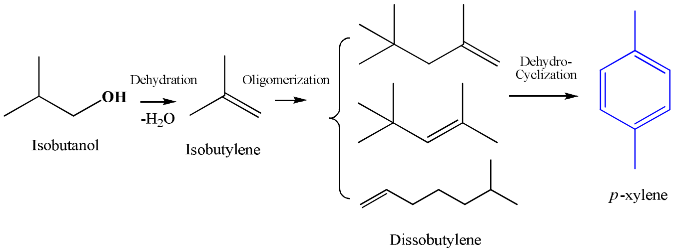
Recently, Pacheco et al. synthesized PTA with ethylene and oxidized derivatives of HMF via Diels-Alder reactions over solid Lewis acid catalysts.[200] The conversion of partially oxidized HMF, methyl 5-(methoxymethyl) furan-2-carboxylate, reached 26% with 81% selectivity of methyl 4-(methoxy-methyl)benzenecarboxylate (MMBC) over Zr-Beta catalysts at 463 K for 6 h. The MMBC could be further converted to PTA with oxidation process. This process obviates the hydrogenation of HMF to DMF, and accordingly is more atomic economic. However, the reaction efficiency and products selectivity need to be further improved.

High yields of *p*-xylene have been obtained from DMF and ethylene/acrolein over different zeolite catalysts. However, it is still a challenge to obtain low cost HMF from cellulosic biomass. The feasibility of this process is highly dependent on the cost of HMF.

3.3 Synthesis of *p*-xylene from isobutanol

With the rapid development of bio-refinery, fermentation of biomass to isobutanol has been applied at pilot scales. The first plant for bio-isobutanol production was set up in Luverne, USA, with a nameplate capacity of 18 million gallon per year.[201, 202] Isobutanol is an important intermediate for producing fuels and chemicals. It can be directly blended with gasoline to be used as fuel. Compared with ethanol, the mostly used blender, butanol has higher blending volume and energy content. Additionally, it could be used as a platform chemical for producing important chemicals, such as *p*-xylene.[203]

The synthesis of *p*-xylene from isobutanol was first developed by Gevo Inc. in USA.[204] As shown in Scheme 8, this process includes three steps: dehydration of isobutanol to isobutylene, oligomerization of isobutylene to dissobutylene, and dehydrocyclization of dissobutylene to *p*-xylene. The dehydration of isobutanol was conducted at 573-623 K in gas phase by using catalysts of BASF-AL3996. The isobutanol conversion and isobutylene yield were higher than 99% and 95%, respectively. The obtained isobutylene stream was then pumped into a fixed-bed oligomerization reactor loaded with commercial ZSM-5 catalysts. In consideration of isomerization and recycle back process, the overall stream conversion and the yield of dissobutylene reached 99% and 89%, respectively. The resulting dissobutylene stream was finally fed into a fix-bed reactor loaded with catalysts of chromium oxide doped alumina (BASF D-1145E $^{1/8}$) at 773-823 K, and produced *p*-xylene with 75% selectivity and hydrogen gas as a by-product. In view of the whole process from isobutanol to *p*-xylene, the yield of *p*-xylene was 18.7%, and by-products were hydrogen, C12 compounds, isobutylene and dissobutylen. At the end of 2011, Gevo Inc. announced an agreement with Coca-Cola to produce renewable *p*-xylene from biomass based isobutanol. Two years later, renewable *p*-xylene was reported to be sold to Toray.[205] Lin et al. investigated the techno-economic analysis for this process. The minimum price for biobased *p*-xylene from isobutanol was $3481/metric ton even after supplementing the values of some byproducts, which is still much higher than petroleum based *p*-xylene (*ca.* $1600/metric ton). The economics of the process might be improved with the development of biocatalyst for isobutanol production. The sensitivity analysis found that the cost of biomass is 46.2% of the operating cost.[206]



Scheme 8 Synthesis of *p*-xylene from isobutanol.

Besides isobutanol, acetic acid was also employed as a feedstock for *p*-xylene synthesis via the intermediate of isobutene. Over $Zn_xZr_yO_z$ catalysts, acetic acid was converted into isobutene with 57% selectivity. The isobutene could be oligomerized and dehydrocyclizaed to *p*-xylene following a method similar to that of Gevo Inc.[207]

Even though Gevo Inc. has produced the bio *p*-xylene from isobuanol, there are still notable problems existing in the economic feasibility. The feedstock employed for fermentation is starch, which is competitive to food supply and limits the economics of the whole *p*-xylene production. The prospect of this process is highly dependent on the development of biocatalyst and the usage of much cheaper feedstock such as cellulosic biomass.

3.4 Synthesis of *p*-xylene via pyrolysis or reforming process

Pyrolysis is the thermal disintegration of organic materials, including biomass derived chemicals, sugars, lignin and lignocellulosic biomass, into solid, liquid and gas at modest temperatures, which has tremendous prospective due to its feedstock compatibility, simplicity of process and low capital investments.[208, 209] With the rapid development of catalysis, a variety of technologies such as catalytic fast pyrolysis (CFP) have been developed, and high yield of valuable chemicals and fuels could be obtained from biomass.[210-212]

In the past decade, considerable efforts have been made to convert biomass into aromatic products such as *p*-xylene with novel catalysts and technologies.[213, 214] Catalytic pyrolysis integrates the biomass pyrolysis with in situ upgrading technique, and the quality of products is improved correspondingly. The yield of aromatic products is greatly affected by the mass transfer of feedstock.[215] For instance, Carlson et al. conducted catalytic pyrolysis of raw biomass, i.e., wood sawdust, with three different reactors: a bench scale bubbling fluidized bed reactor, a fixed bed reactor and a semi-batch pyroprobe reactor. The aromatic yield was maximized to 11% carbon over the catalysts of HZSM-5 in a fluidized bed reactor.[216] Nevertheless, about 30% of carbon was transformed to coke during the reactions. Therefore, some typical compounds, such as platform chemicals, bio-oils, cellulose and lignin, were firstly employed as feedstock for *p*-xylene synthesis. Vispute et al. employed different bio-oil as feedstock for synthesis of olefins and aromatic compounds over catalysts of Ru/C and zeolites. Maximum yield of aromatic compounds was 21.6% with 31.3% selectivity to xylene.[217] Karanjkar et al. studied the CFP of cellulose at 773 K by using a ZSM-5 catalyst in a bubbling fluidized bed reactor. The aromatics yield was enhanced to 39.5% by optimizing the catalyst bed height, fluidization gas and bubble sizes.[218] Zhou et al. co-pyrolyzed cellulose with low-density polyethylene, and obtained *p*-xylene at a yield of 5.6% with selectivity of 75.2%.[219] Thring et al. studied the conversion of lignin–acetone solution at 773-923 K over ZSM-5 catalysts with a fix-bed reactor. The aromatic yield according to the liquid products reached 89.4%.[220]

The selectivity of *p*-xylene could be adjusted by modifying the structure of catalysts. Cheng et al. designed a zeolite catalyst, ZSM-5 modified with tetraorthosilicate by chemical liquid deposition (CLD), for biomass pyrolysis. The CLD method narrowed the pore openings of ZSM-5 catalysts, caused remarkable effect of space confinement and increased the *p*-xylene selectivity from 32% to 96% in the conversion of 2-methylfuran and propylene.[211, 221, 222] In a further study, they employed pinewood as feedstock for CFP over spray-dried gallium catalysts. The aromatics yield reached 19.5% with 11% yield of *p*-xylene. CFP technology was also used for pine wood, alcohols (methanol, 1-propanol, 1-butanol and 2-butanol) and their mixtures over ZSM-5 catalysts in a bubbling fluidized bed reactor, and the aromatics yield reached 21.4% at 723 K with a WHSV of 0.63 h^{-1}.[223] In 2012, Anellotech was licensed with this technology for *p*-xylene production from non-food biomass.[224]

Although lignocellulosic biomass could be converted as a whole to aromatic compounds, the mechanisms of sugar and lignin conversion are quite different. For the sugars conversion, they are cracked to acids, alcohols, esters and ketones, which further decompose to olefins and then undergo Diels-Alder reactions to produce aromatics. [225, 226] The formation of aromatics from lignin lies in the decomposition and reforming of lignin unites.[227] Lignin is cleaved to BTX. After further reforming these obtained unites with shape-selective zeolites, *p*-xylene could be formed.[228, 229]

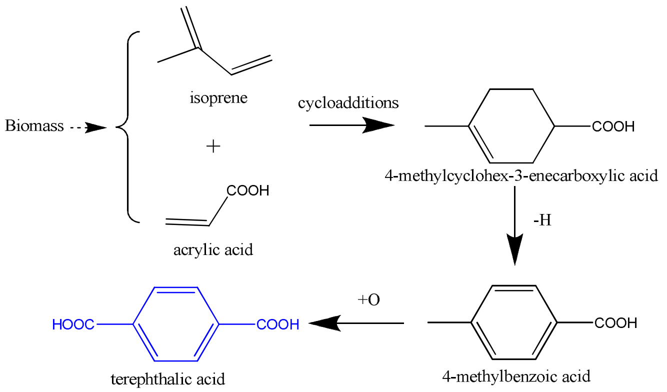
Pyrolysis of biomass to *p*-xylene is a promising technology for a large scale application owing to the rapid development of fast pyrolysis technologies. Nevertheless, a wide variety of products are produced during biomass pyrolysis and the *p*-xylene must be purified from these downstream. Thereby, it is still a challenge to controllable synthesis of *p*-xylene with high yield and selectivity. More robust shape-selective and multi-functional catalysts should be developed for enhancing the *p*-xylene selectivity.

Another strategy for green aromatic compounds synthesis is reforming of sugars or polyols. For instance, Kunkes et al. converted sorbitol or sugars to primarily hydrophobic alcohols, ketones, carboxylic acids, and heterocyclic compounds over a Pt-Re catalyst. These intermediates underwent self-coupling reactions, and afforded 38.3% alkylated aromatics over HZSM-5 catalysts at 673 K.[230] Tan et al. investigated the aqueous catalytic reforming of sorbitol, and 34.4% yield of aromatics was achieved when 3 wt% Ni was loaded on HZSM-5 zeolite.[231]

Virent integrated the aqueous phase reforming (APR) technology with modified conventional catalytic processing to form the BioForming® technology for biomass conversion. They first convert aqueous carbohydrate solutions into a mixture of chemical intermediates including alcohols, ketones, acids, furans, paraffins and other oxygenated hydrocarbons, and then the mixture is transformed over modified ZSM-5 catalyst to obtain the gasoline blend stock which has a high content of aromatics.[232-236] Virent commenced collaboration with Coca-Cola in 2011 for the development of bio-based *p*-xylene technology. In 2015, they announced that BioFormPX® *p*-xylene was used in the world's first demonstration scale production (Wisconsin demonstration plant) of bio-PET.[237]

3.5 Synthesis of PTA from isoprene and acrylic acid

Bio-isoprene is produced from sugars fermentation by Gram-positive or Gram-negative bacteria. With the modification of bacteria, 10.7% of isoprene was obtained from glucose after a fed-batch fermentation for 59 h.[238, 239] On the other hand, three processes, i.e. lactic acid process,[240-243] glycerine process [244] and 3-hydroxypropionic acid process,[245] have been developed for the production of bio based acrylic acid. Therefore, isoprene and acrylic acid could be used as potential feedstock for PTA synthesis.



Scheme 9 Synthesis of PTA from isoprene and acrylic acid (modified from ref. [246])

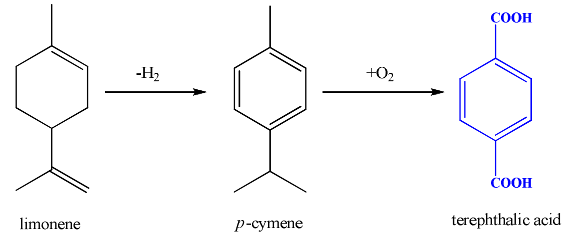
The process for PTA synthesis from isoprene and acrylic acid is shown in Scheme 9. Conversion of isoprene and acrylic acid to PTA follows sequential reactions of Diels–Alder reaction, dehydro-aromatization and oxidation reaction. Wang et al. studied the dehydro-aromatization reaction with different substrates.[246] Under mild conditions, the desired aromatic products reached extremely high yields of 83-100% by using sulfuric acid as an oxidant. The resulted 4-methylbenzoic acid was further oxidized with $KMnO_4$-NaOH for 2 h, giving 95% PTA yield. Miller et al. employed Lewis acid catalyst for the cycloaddition of isoprene and acrylic acid. The yield of 4-methylcyclohex-3-enecarboxylic acid reached 90% after 24 h reaction at room temperature with $TiCl_4$ as a catalyst. They found that low reaction temperature preferred the formation of 4-methylcyclohex-3-enecarboxylic acid at the expense of reaction efficiency. After vapour-phase aromatization and oxidation steps, PTA was obtained.[247, 248]

Differing from the routes 1 to 4, this method reserves the carboxy group of starting material in the final PTA after three reactions, and accordingly has a very high atom economy and much high selectivity to the target product. On the other hand, the flaws of this process are also evident. The feedstock of isoprene and acrylic acid are high value-added chemicals, and the catalysts used in the reactions are strongly corrosive homogeneous catalysts. Hence, to obtain cheap feedstock and explore more environmental friendly and robust heterogeneous catalysts are main hurdles that need to be overcome.

3.6 Synthesis of PTA from limonene

Limonene can also be used as a precursor for synthesis of PTA, which can be extracted from orange peels. The structure of limonene is very similar to *p*-xylene, which makes it a candidate feedstock for PTA synthesis. As shown in Scheme 10, the limonene can be dehydrogenated to yield aromatic *p*-cymene and then oxidized to PTA.[33, 37, 249]

This route has only two steps with *p*-cymene as an intermediate, which is convenient for PTA synthesis. However, the production capacity of limonene is limited, and limonene has many applications such as food and perfume additives. Therefore, to get cheap and large amounts of limonene feedstock are key issues for the application of this route.



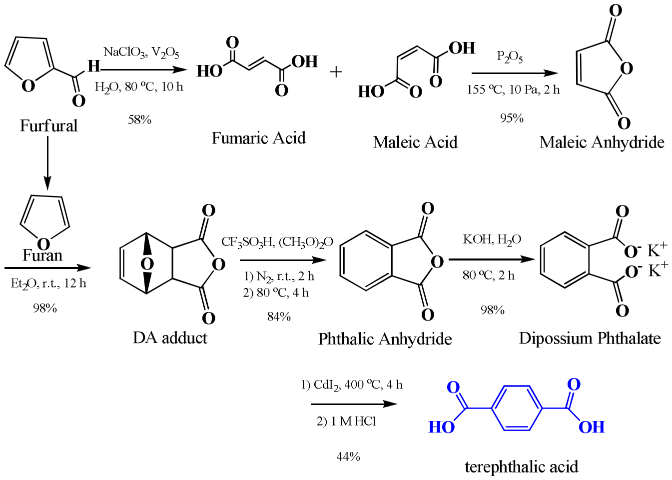
Scheme 10 Synthesis of PTA from limonene (modified from ref. [33])

3.7 Synthesis of PTA from furfural

Furfural is also an important industrial chemicals derived from biomass, which is produced by hydrolysis and dehydration of xylan in lignocellulosic biomass. The annual production of furfural reached 0.5-1 million tonnes.[250, 251]

Recently, a route for the synthesis of PTA from furfural was reported by Tachibana Y. et al.[252] As shown in scheme 11, this route includes six steps, namely, oxidation of furfural to fumaric acid and maleic acid, dehydration of fumaric acid and maleic acid to maleic anhydride, Diels-Alder (DA) reaction of anhydrous maleic acid and furan to DA adduct, dehydration of the DA adduct to phthalic anhydride, hydrolysis of phthalic anhydride to dipotassium phthalate, transfer reaction and acidification of dipotassium phthalate to terephthalic acid. By integrating these steps, PTA could be synthesized from furfural with 100% biobased carbon as measured by accelerator mass spectroscopy.

This route employed homogeneous and corrosive catalysts with multi steps, which significantly decreased the PTA yield to less than 20% from furfural. Effective integration of these multi steps and development of novel heterogeneous catalysts, especially for steps 1 and 6, are crucial targets that need to be realized for further application.



Scheme 11 Synthetic route to biobased TPA from furfural (modified from ref. [252])

3.8 Comparison of different biomass-based routes for PTA synthesis

For comparison, the yield of products, advantages and drawbacks of each route are listed in Table 4. Synthesis of *p*-xylene from HMF receives the highest yield of 85%. However, the cost of

HMF is relative high, which greatly affects the economic viability of this process. The bio-ethylene and furfuran routes are novel strategies for PTA synthesis. The yields of products are relatively high, but it comprises multi steps under harsh reaction conditions, which increases the difficulty for its application. It is a challenge to synthesize PTA from limonene, isoprene and acrylic acid due to the high cost of feedstock. Even though the yield of *p*-xylene is less than 20% for isobutanol approach, the feedstock of isobutanol is abundant in Gevo Inc. Synthesis of *p*-xylene via pyrolysis or reforming is a very promising technology. The BioForming® *p*-xylene has been synthesized for producing 100% green PET bottle for Coca-Cola. These seven routes have made rapid progresses, and some of which showed great commercial prospective. However, their feasibilities are still dependent on the economic evaluation.

Table 4 Comparison of typical routes for *p*-xylene synthesis from biomass[a]

Feedstock	Yield /%	Advantages	Disadvantages
ethanol	49[b]	High yield	Low efficiency, harsh conditions
HMF	85[b]	High yield	High cost of feedstock
isobutanol	18.7	Feedstock available	Economics evaluation
biomass	11	Low selectivity	Easy operation
isoprene and acrylic acid	78[b]	High yield	Limited feedstock resource
limonene	--	Short pathway	Limited feedstock resource
furfural	19.5[b]	Solo feedstock with certain market	Multi steps with harsh reaction conditions

[a] the product for routes from isoprene and acrylic acid, limonene and furfural is PTA; [b] the yield was carbon yield, which was calculated based on the maximized yield of each reaction step ever reported.

4. Concluding remarks and prospects

Efficient and environmentally benign transformation of biomass to PET monomers is an important but challenging work. In the past decade, great advances have been made in the bio-catalysis and chemical conversion, and several routes have been developed. Some of routes have been commercialized with "drop-in" replacements of fossil based products.

For EG synthesis, ethanol, glycerol, sorbitol, sugars and (hemi)cellulose can be used as potential intermediates or feedstocks. Table 5 lists the key steps and status of each route. The approach to synthesize EG from ethanol is very attractive due to the rapid development of sugar or cellulosic ethanol. It has been commercialized in Brazil with the support of Coca-Cola to take advantage of the abundant sugar production. Hydrogenolysis of glycerol is another way to produce EG, but it has the drawbacks of limited resource of glycerol and the low atom economy. Synthesis of EG from sorbitol or sugars is very attractive, which has been commercialized in China. Even though the dominate product is 1,2-PG for glycerol and sugar-sorbitol conversion, EG is a main co-product during the hydrogenation reactions. These processes could be regarded as candidate methods for green EG synthesis. DLEG process is a newly emerging but promising route, which has the advantages of high EG selectivity, high atom economy, one-pot process and co-conversion of hemicellulose and cellulose. From the technique and economic point of view, the challenge of this route is the reaction efficiency and the selective separation of (hemi)cellulose from lignocellulosic biomass.

There are at least seven approaches for PTA synthesis from biomass. Among these approaches, the synthesis of PTA from ethylene via ethanol as an intermediate has the same problems with EG synthesis from ethanol. Moreover, the selectivity to *p*-xylene is very low after a series of reactions, which needs to be improved in the future study. The HMF approach is a promising process due to the hot investigation on HMF production and its utilization. The feasibility of this approach is determined by the techno-economic evaluation of the whole process. Recently, *p*-xylene is produced from isobutanol, which has been produced in pilot scale. Nevertheless, there are more than five steps for PTA synthesis from isobutanol, which greatly decrease the reaction efficiency and product selectivity. Catalytic pyrolysis or reforming process is another route that receiving a lot of interest. One of the advantages of this route is that it starts with low cost lignocellulosic biomass and directly convert it into aromatics in a single catalytic step. However, it is still a challenge to get high *p*-xylene selectivity. The synthesis of PTA from isoprene and acrylic acid has advantages of high efficiency and short reaction steps, but has the drawbacks of homogenous catalysts and high value of feedstock. The PTA could be obtained through dehydration and oxidation of limonene, but the feedstock of limonene is value-added. The synthesis of *p*-xylene from furfural is the latest developing approach, which produces bio-PTA from furfural through organic synthetic procedures by homogeneous catalysts.

Table 5 Comparison of different approaches for synthesis of EG and PTA from biomass

Biomass derived feedstock	Reaction steps from biomass	Technology status	Company
ethanol	dehydration, oxidation, hydration	Commercial	JBF Industries Ltd.（500 kT）;GTC（120 kT）

EG	glycerol	hydrogenation	--	--
	sugar/sorbitol	hydrogenation	Commercial	Changchun Dacheng Industrial Group Company Ltd. （200 kT）
	raw biomass	hydrogenation	Laboratory	--
PTA	ethanol	trimerization, disproportionation, Diels-Alder reaction, dehydration, oxidation	Laboratory	--
	HMF	hydrogenation, Diels-Alder reaction, dehydration, oxidation	Laboratory	Micromidas, UOP
	isobutanol	dehydration, oligomerization, dehydrocyclization, dehydration, oxidation	Pilot	Gevo, Inc.
	--	pyrolysis	Demonstration	Anellotech, Inc. Virent
	isoprene and acrylic acid	Diels–Alder reaction, dehydro-aromatization and oxidation	Laboratory	--
	limonene	dehydrogenation, oxidation	--	--
	furfural	oxidation, dehydration, Diels-Alder reaction, hydrolysis	Laboratory	--

With the rapid development of biomass conversion, EG and PTA could be obtained from the intermediates as we list in Table 5. However, the feasibility of these routes is still dependent on the cost of feedstock, catalysts development and the economics of these processes. The following aspects should be studied to continue to develop these technologies.

1). Develop stable and water tolerant heterogeneous catalysts. The conversions of glycerol, sugars or cellulosic biomass to EG are usually conducted under hydrothermal conditions. The fierce reaction conditions limit the application of most transition metal oxides due to their poor water tolerance. Moreover, for non-noble metal catalysts, the strong adsorption of some reaction intermediates, metal leaching and particles aggregation may also decrease the stability of catalysts.

The conversion of biomass to PTA is a complex multi-step process. To improve the reaction efficiency and product selectivity, homogeneous catalysts should be replaced by heterogeneous catalysts and multifunctional catalysts should be designed to minimize the reaction steps.

2). Conversion of non-edible biomass. That is the cheapest renewable feedstock that can be used. Most of the existing routes for EG and PTA synthesis employ sugars as starting materials. For some specific areas in the world, it is an optional technology for the utilizing local abundant crops. Nevertheless, it is still food competitive, and should be gradually replaced by the conversion of lignocellulosic biomass with the development of bio and catalytic catalysts. To obtain the intermediates or platform chemicals such as ethanol, sugars, isoprene and acrylic acid, pretreatments are always employed to unlock the structure and increase the accessibility of biomass. Nowadays, pretreatment processes are still regarded as the most expensive process for cellulosic biomass utilization. Therefore, how to isolate the three components of cellulose, hemicellulose and lignin with low-cost methods might be one of the most important issues for scaling up the conversion of biomass.

3). Integration of biological and chemical process for biomass conversion. As we can see from these routes for EG and PTA synthesis, biological catalysts are always employed for raw biomass conversion due to its compatibility of feedstock. More important, the biocatalysts are tolerant to lignin, sugars or activated cellulose could be totally converted even in the presence of large amounts of lignin. Differently, chemical reactions are usually conducted at harsh conditions with high reaction efficiency. Especially for the conversion of platform chemicals, the reaction rate and products selectivity could be turned by modifying catalysts. Biological and chemical catalysts have been integrated for EG and PTA synthesis, and showed promising results, e.g., the conversion of biomass to EG with ethanol as intermediates, conversion of *p*-xylene from isobutanol. Hence, integration of biocatalysis and chemical conversion may be an optional way for conversion of raw biomass to PET.

4). Politics of different countries and newly emerging energy resources. The application of EG and PTA synthesis from biomass are also strongly influenced by the governmental policies. Take USA and China as examples, the cellulosic ethanol is encouraged with certain tax exemption or subsidy from government. The green chemicals are also influenced by new energy resources like shale gas in USA.

Up to four routes for EG and seven routes for PTA synthesis from biomass have been developed. Even though most routes confront various problems and some of them are rather challenging, the progresses in these methods still shed light on the potential synthesis of green PET from biomass. With the endeavours of world-wide researchers and governments, the biomass derived PET is being rapidly developed, and it would gradually "drop-in" replace the fossil-based resin.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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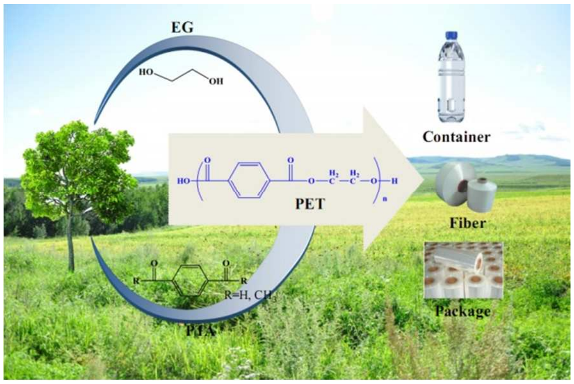
Table of Content



This review presents recent advances in typical routes for drop-in replacement of Poly(ethylene terephthalate) monomers from biomass.