Catalytic Conversion of Alcohols into Value-Added Products

R. Vinayagamoorthi, B. Viswanathan, and K. R. Krishnamurthy

Abstract Alcohols belong to an important class of oxygenates, containing highly versatile hydroxyl (–OH) functional group(s) which are capable of undergoing a variety of chemical transformations, yielding fuels, fuel additives and a wide range of highly useful chemicals and chemical intermediates. Production of methanol, bioethanol and other higher alcohols in plenty, through various biomass conversion processes, has rendered them renewable and carbon-neutral in character and highly useful as platform chemicals. Novel catalytic processes for the conversion of aliphatic C_1-C_4 alcohols to C_2-C_4 olefins/building block chemicals, like ethylene, propylene, isobutene and butadiene, and oxygenates like aldehydes, esters and ethers and gasoline range hydrocarbons have been developed. Catalytic coupling of ethanol to higher alcohols followed by dehydration, oligomerization and hydrogenation to yield jet fuel and middle distillates results in the production of low-carbon renewable/sustainable fuels. Steam reforming and aqueous phase reforming of alcohols to produce hydrogen is yet another process option available for the transformation of alcohols that has several advantages over conventional, non-renewable methane steam reforming. Significant progress has been reported in the catalytic α-alkylation of ketone esters and amides with alcohols and aldol condensation of alcohols with other oxygenates like acetone/ketones. Catalytic upgradation of biomass-derived glycerol, furfuryl alcohol and sugar-derived alcohols like sorbitol, mannitol and xylitol results in a range of value-added products. The origin of such processes, process chemistry, development of catalysts, recent advances and future trends are covered in this chapter.

Keywords Biomass conversion · Biofuels · Sugar alcohols · Furfuryl alcohol · Glycerol

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1 Introduction

In the journey towards clean energy and environmental sustainability, identification of biomass as an alternate, renewable and sustainable resource and the advent of biomass conversion processes for the production of fuels and chemicals are the two important milestones [1–5]. Abundant availability of various types of biomass [6–8] and the development of a series of biomass conversion processes, through homogeneous, heterogeneous and enzymatic catalytic routes, have opened up a new avenue of research, full of challenges and enormous opportunities [9–12]. Through sustained research efforts, spread over more than three decades, a well-defined road map in this vital area has been drawn up. Emergence of the concept of *biorefinery* [13–15], akin to the petroleum refining/petrochemical plants based on fossil resources [16, 17], was the first step in this direction. As the nodal entity, biorefinery provides a structured approach, oriented towards the development of biomass conversion processes for practical applications. Different types of lignocellulosic biomass, which are useful as feedstock for the biorefinery, in general, consist of three major components [18], namely, cellulose (34–54%), hemicellulose (19–34%) and lignin (11–30%). Being complex in character, it is necessary that the biomass is first converted into relatively simple and active intermediates or platform chemicals, which can undergo further transformations in a facile manner, into value-added products with wider applications (Fig. 1).

In an effort to drive focused research work in the area of biomass conversion, the US Department of Energy (DOE) in 2004 identified a set of 12 platform chemicals,

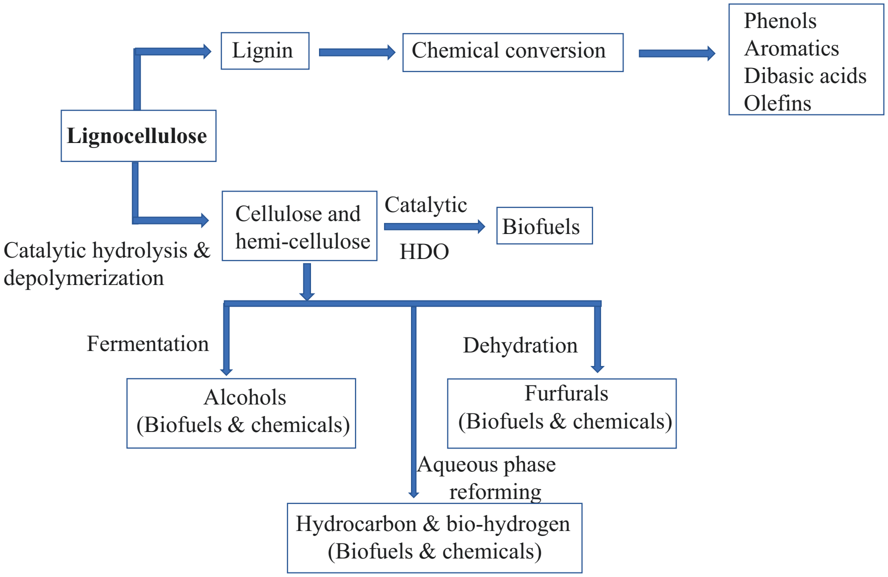


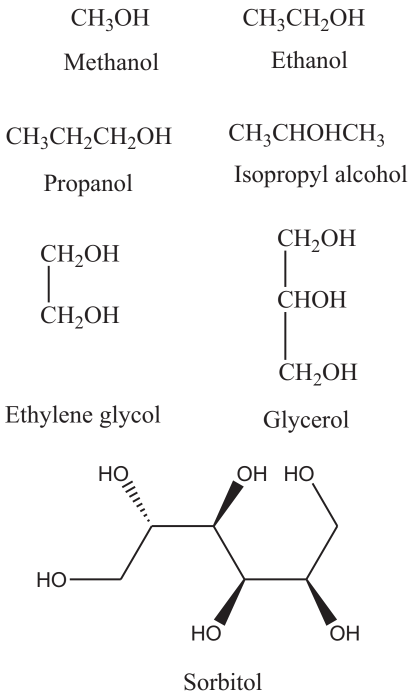
Fig. 1 Primary processing of biomass in biorefinery (Adapted from Kohli et al. [19])

namely, succinic, fumaric and maleic acids, 2,3-furan dicarboxylic acid, hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxy-butyrolactone, *glycerol, sorbitol and xylitol/arabinitol*, based on the importance of the final products derived from them, by utilizing the existing conversion processes [20]. With the development of novel catalysts and processes specifically for biomass conversion, a greater number of platform chemicals were identified, and the list was subsequently updated in 2010 to include *ethanol*, *furfural*, hydroxy methyl furfural, 2,5-furan dicarboxylic acid, lactic acid and isoprene, besides those considered in the earlier list [21]. Development of sustainable chemistry/processes now revolves around these platform chemicals for conversion to end products, which were otherwise being produced from fossil resources. *It is pertinent to note that as many as five biomass-derived alcohols are considered as platform chemicals.* Both sugar/starch-based and lignocellulosic feedstock-based biorefineries that follow biochemical (fermentation), thermochemical (gasification of biomass to syngas) and hybrid syngas-biochemical routes [22–25] produce a range of alcohols, rendering them as abundantly available, low-cost and carbon-neutral platform chemicals. In this scenario, several novel catalytic processes for the conversion of alcohols into biofuels and value-added products have emerged. Salient features of such bio-alcohols-based processes, process chemistry, development of catalysts and future trends are described in this chapter.

2 Chemistry of Alcohols

Alcohols (R-OH) belong to an important class of oxygenates, containing highly versatile hydroxyl (–OH) functional group(s) which are capable of undergoing a variety of chemical transformations involving cleavage of O-H or R-O bonds [26]. Variations in the molecular structure (primary, secondary and tertiary alcohols) and nature (mono-, di-, tri- and polyhydric alcohols) (Fig. 2) govern their reactivity and product selectivity for various reactions like oxidation, reduction, esterification, dehydration, dehydrogenation, nucleophilic substitution, etherification and cyclization. With the growing importance of biomass conversion processes, several other reactions of alcohols, like aldol condensation with aldehydes and ketones, acetalization, alcohol coupling and aromatization reactions are being pursued [27]. Based on the carbon number, alcohols can be divided broadly into different groups, C_1–C_2 alcohols (methanol and ethanol), C_3–C_5 alcohols (1-propanol,1-butanol, 1-pentanol) and C_6–C_{22} long-chain alcohols (2-ethyl hexanol, 1-decanol) and sugar alcohols (sorbitol, mannitol). Besides their applications as fuels/fuel additives, alcohols, in general, are used as feedstocks for numerous processes related to a wide spectrum of industrial sectors, chemical, petrochemical, polymers, pharmaceutical, fine chemicals and agro-chemicals, detergents, personal care products, lubricants and industrial solvents for various applications (inks, paints, coatings, etc.).

Fig. 2 Types of alcohols



3 Production and Applications of Alcohols

Methanol, with an estimated annual consumption of 97 MMT (million metric tons) during 2019 [28], is one of the most important bulk chemical and raw materials used for the production of a number of value-added chemicals (Fig. 3). Leading global companies engaged in methanol production are BASF SE, Methanex Corporation, Mitsubishi Chemical, Mitsui & Co., Ltd. and Petroliam Nasional Berhad (Petronas). Current industrial process for the manufacture of methanol is based on fossil-derived (natural gas, coal) syngas ($CO + H_2$) as raw material, mostly through the low-pressure process developed by ICI (now Johnson Matthey) operating at 35–54 bar pressure and in the temperature range of 200–300 °C [29]. Details on 100 years of history of industrial methanol synthesis process and catalysts, the developments starting from the wood-based process and the classical high-pressure BASF catalytic process down to the recent ones, major products from different methanol conversion processes and their applications and its fuel characteristics and applications as fuel/fuel additives have been covered in exhaustive reviews [29–31].

As on date, investigations on fundamental aspects and development of superior methanol synthesis catalysts/process continue to be active areas of research. Such studies are highly relevant, especially in the current context, wherein the emphasis is on the use of the most abundant greenhouse gas (GHG) CO_2 in the place of CO

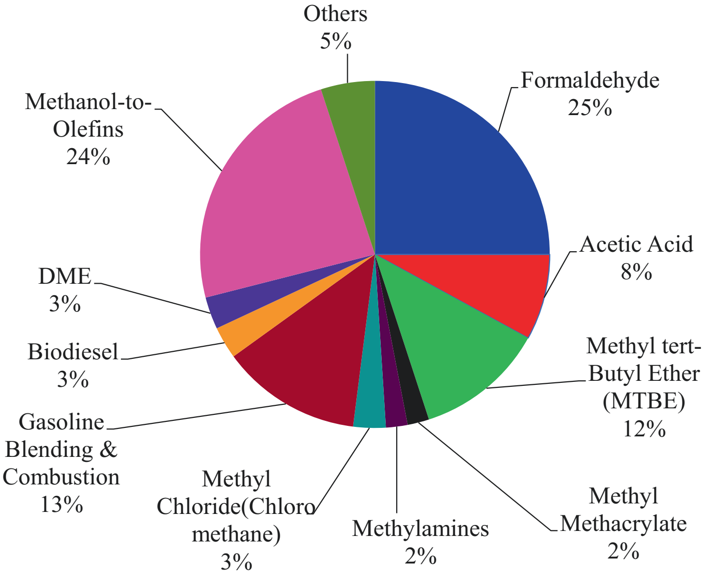


Fig. 3 Consumption pattern for methanol, product-wise in 2019 [28]

Table 1 Novel processes under development for the synthesis of renewable methanol

Company/process	Raw material
BioMCN, Netherlands	Crude glycerine, green gas, biomass, CO_2
Enerkem, Canada	Municipal solid waste
Carbon Recycling International, Iceland	CO_2 from geothermal power station and renewable H_2 by electrolysis using geothermal and hydroelectricity
Chemrec AB, Sweden	Gasification of black liquor from paper/pulp industry
Vamlandsmetanol, Sweden	Gasification of forest residue biomass
Maverick Synfuels	Biomass-derived syngas

and moving towards developing sustainable, low-carbon processes, using renewable biomass resources. The basic attributes of *green/renewable methanol* are (1) use of renewable carbon source/waste product, (2) the hydrogen used is not produced from fossil fuel sources and (3) the energy used is generated from renewable sources [32–34]. Table 1 gives a list of such efforts for developing processes that utilize syngas derived from renewable biomass resources, utilize carbon oxides from industrial waste gases and municipal solid wastes and use renewable hydrogen by electrolysis [35]. The first three processes are in the advanced stage of development. Compared to fossil-based, renewable methanol production results in 65–90% reduction in CO_2 emission, depending on the feedstock and process.

Synthesis of methanol via enzymatic routes, by oxidation of methane by methylotrophs (*Methylosinus trichosporium*) and ammonia-oxidizing bacteria (*Nitrosomonas* spp.), both using the enzyme methane monooxygenase, has been reported [36–40]. However, the maximum methanol concentration of 1.1 g/L makes it unviable economically. Tyurin and Kiriukhin [41] could achieve more than 70 g/L methanol from a 20% CO_2/80% H_2 gas mixture in continuous fermentation using an acetogenic *Clostridium*. The process could be a totally sustainable one, when CO_2 from any waste gas stream and renewable hydrogen from water via photovoltaic-powered electrolysis are used.

With the addition of a number of renewable resources as raw materials, the cost of methanol as feedstock for chemicals and fuels is set to become competitive and hence the products there from (Fig. 4). With the continued growth of petrochemicals, increasing demand for blending in transportation fuels/additives and use as alternative fuel, consumption of methanol is expected to grow. Besides, utilization of methanol for production of ethylene and propylene by MTO process has increased significantly, from 6% in 2011 [42] to 24% in 2019 [28], indicating a shift away from energy-intensive steam cracking process and fossil-based resources for ethylene and propylene production.

Ethanol—Unlike methanol and most of the other alcohols, almost all ethanol is manufactured worldwide by fermentation process that has undergone several improvements over the years to increase the efficiency and lower the cost of production [43–46]. Broadly, three bio-based feedstocks, namely, (1) sugars (i.e. sugar cane, molasses, fruits, etc.), (2) starches (i.e. grains such as maize, root crops such as cassava) which are to be first hydrolysed to fermentable sugars, and (3) cellulose (i.e. woody material, agricultural waste, black liquor from pulp and paper) which again needs to be converted to sugars by the pretreatment with mineral acids (e.g. acid or enzymatic hydrolysis), are being used. Historical developments in the processes for the production of ethanol through the first-, second-, third- and fourth-generation bioethanol, utilizing different feedstocks/routes, have been covered extensively in literature [47–51]. A simplified representation of the bioethanol

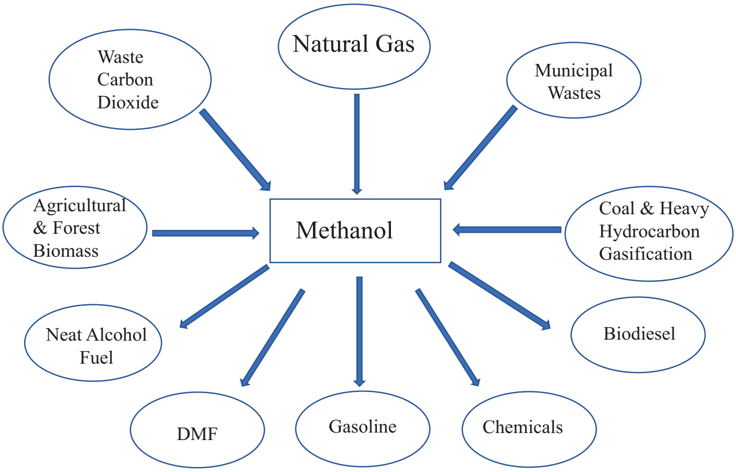


Fig. 4 Methanol – raw materials and major products

manufacturing processes through the generations and the primary process steps involved therein are given in Fig. 5 [49].

Global ethanol production has increased steadily from around 75 billion litres in 2007–2009 to 160 billion litres in 2019 [52] with coarse grains and sugar cane being the major feedstock and the USA and Brazil making up >80% of global production (Fig. 6). Corn/grains and sugar cane are food based and specific to the USA and Brazil. Amongst the feedstocks used for bioethanol production, non-food lignocellulosic biomass is the most promising one, due to its abundancy, low cost and availability of appropriate process technology. However, the cellulosic process for the production of bioethanol is complex in nature involving several steps, and hence its price as biofuel is not competitive in comparison with fossil fuels and its utilization as raw material for the production of bio-derived ethylene. Recently an attractive strategy [53] to lower the cost has been proposed, wherein besides ethanol, other value-added chemicals could be produced as co-products.

Of recent, fermentation processes that use syngas derived from biomass, industrial wastes and municipal solid wastes are being explored vigorously due to the potential advantages in cost and low-carbon character [54]. Gas fermentation technologies at pilot scale and demonstration plants have been set up by companies Coskata, INEOS Bio and LanzaTech [55, 56] with the ultimate objective of commercial production. Availability of bioethanol in plenty from various biomass resources and development of processes for ethanol conversion to building block chemicals and key chemical intermediates (Fig. 7) have rendered it as a highly valuable and versatile platform chemical [56].

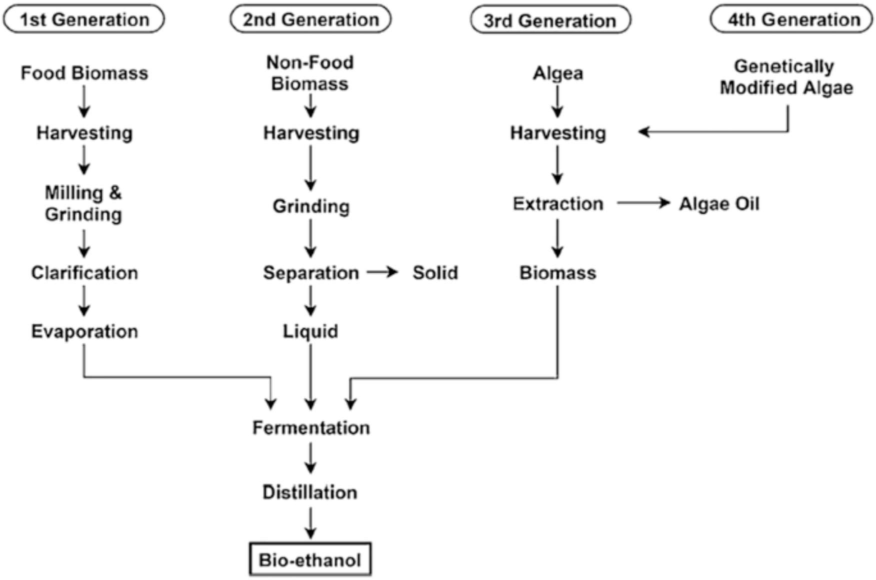


Fig. 5 Process steps involved in the production of bioethanol (Reproduced from Alalwan et al. [49])

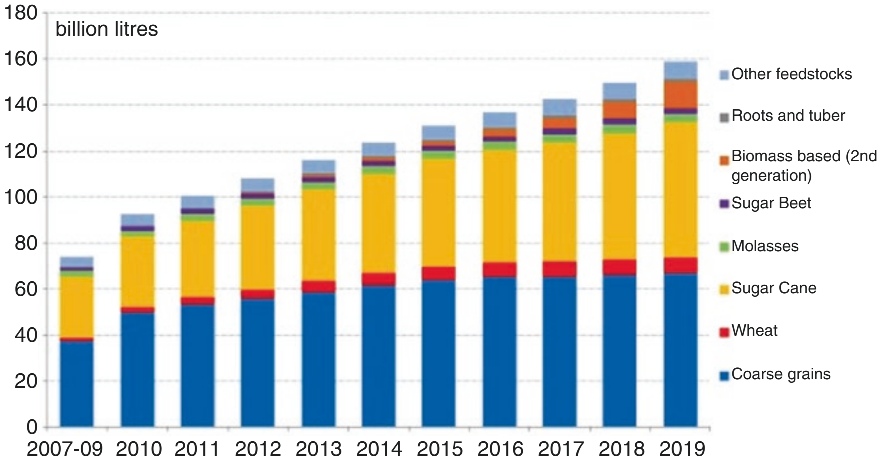


Fig. 6 Global ethanol production (2007–2019) [52]

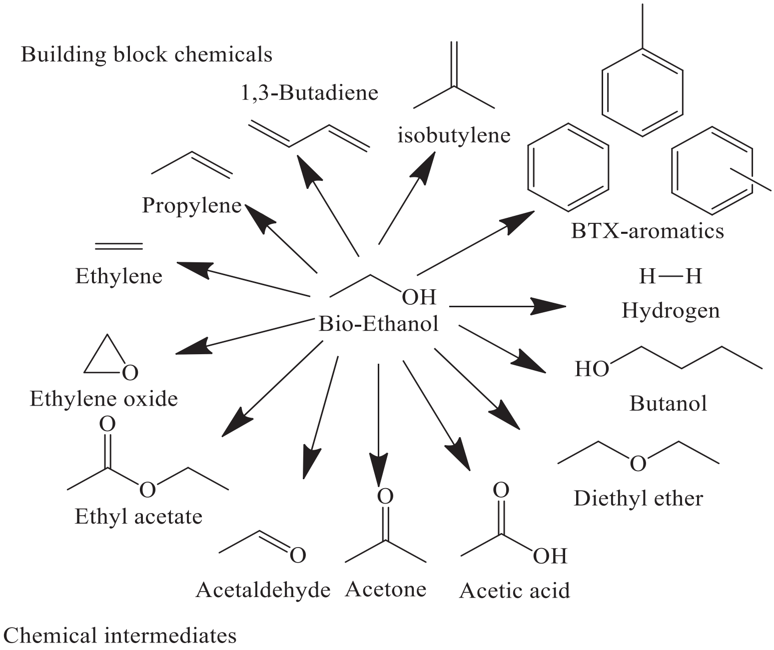


Fig. 7 Bioethanol—a versatile platform chemical (Adapted from Kuhz et al. [56])

Amongst C_3 *alcohols*, *1-propanol* is produced by hydrogenation of propanal, which, in turn, is manufactured from ethylene by hydroformylation process [57]. Attempts have been made for the production by microbial routes [58], and the best yield 10.8 g/L has been realized for the process using a recombinant *E. coli* as host

[59]. 1-Propanol finds applications [57] as a solvent, antimicrobial agent and chemical intermediates for the production of value-added products.

There are two different routes for the manufacture of *isopropanol*, (1) indirect hydration of propylene with H_2SO_4 via a mixture of mono- and di-isopropyl sulphate esters and (2) direct hydration of propylene over an acidic heterogeneous catalyst [56]. Its applications include use as a solvent in inks and surfactants, as a chemical intermediate and as a cleaning fluid [57]. Microbial processes for isopropanol production, including *Clostridium beijerinckii*, engineered *E. coli* and engineered *Clostridium acetobutylicum* [60, 61], have been reported.

C_4 alcohols, namely, *1-butanol (n-butanol)*, *2-butanol (secondary butanol)*, *2-methyl propanol (isobutanol) and 2-methyl 2-propanol (tertiary butyl alcohol)*, are highly versatile in terms of applications as solvents, in manufacturing of chemical intermediates and as fuel additives. Details on the manufacturing of *1-butanol*, *2-butanol and 2-methyl propanol* by conventional chemical as well as microbial routes and typical applications have been described by Kunz et al. [56]. *2-Methyl 2-propanol* (tertiary butyl alcohol) is produced by hydration of isobutylene [62]. Its reaction with methanol/ethanol results in methyl tertiary butyl ether (MTBE)/ethyl tertiary butyl ether (ETBE), useful as octane booster and oxygenate for blending with gasoline. Tertiary butyl hydroperoxide (TBHP) is another useful chemical intermediate.

Amongst C_4 alcohols, *1-butanol* has the unique distinction of being highly useful raw material/chemical and the most efficient gasoline additive. 1-Butanol is considered as the next-generation biofuel [63, 64] with several advantages over ethanol (Table 2), such as higher energy density (29.2 vs. 19.6 MJ/L), lower volatility and solubility in water and non-corrosive nature. Besides, butanol blends well with gasoline and with higher air-to-fuel ratio results in more efficient combustion [65–69]. 1-Butanol finds widespread applications in chemical industry, in the manufacture of butyl acrylate, butyl acetate, glycol ethers and plasticizers and as solvent in the manufacture of coatings, paintings, engineering plastics, super absorbent polymers, adhesives and sealants. With the increase in the consumption of 1-butanol for these applications, its market has been expanding over the years. n-Butanol market, estimated at US$ 3.89 billion in 2016, is projected to touch US$ 5.58 billion by 2022, at a CAGR of 5.9% [70].

Currently, 1-butanol is produced from propylene by the oxo process [71, 72], which is based on the use of the raw material derived from non-renewable resources. Availability of bioethanol in plenty and at low cost has triggered global research

Table 2 Fuel characteristics of 1-butanol vs. other fuels (Adapted from Gautam and Martin [65])

Fuel	Energy density (MJ/L)	Air-to-fuel ratio	Energy content/ Btu/US gallon	Research octane number	Water solubility (%)
Gasoline	32	14.6	114,000	81–89	Negligible
Diesel	35.5	14.7	130,000	nd	Negligible
Butanol-1	29.2	11.12	105,000	78	7
Ethanol	19.6	8.94	84,000	96	100

efforts on the development of sustainable chemical catalytic processes for the conversion of bioethanol to 1-butanol via classical Guerbet chemistry [73, 74]. A number of reviews covering in detail the development of both homogeneous and heterogeneous processes and catalysts for the conversion of ethanol to 1-butanol have been published [56, 75–77]. Several types of heterogeneous catalysts, based on MgO, Mg−Al-O mixed oxides, Cu/CeO_2, basic zeolites, hydroxyapatite, solid acid-supported Cu and alumina- and carbon-supported metal catalysts, in batch and continuous-flow mode, under different reaction conditions, have been explored [77]. 1-Butanol yields in the range 20–30% could be obtained with heterogeneous catalysts [77] along with the formation of C_{4+} alcohols. With Ru-based homogeneous catalysts, n-butanol selectivity as high as 94%, but at very low ethanol conversion of 22% (21% yield of butanol), has been reported [78]. Thus, achieving high yields of 1-butanol remains a challenge. Increase in demand for 1-butanol has led to the revival of one of the oldest known fermentation processes, ABE (acetone-butanol-ethanol) process for production of 1-butanol, using different strains of *Clostridium* sp. with glucose, starch, molasses, corn stover, rice straw and cranny grass as feedstocks [79–81]. Different types of biomass feedstocks, microorganisms, biomass pretreatment methods, extraction methods, genetic engineering techniques like cell recycle and cell immobilization and strategies to minimize product inhibition have been adopted to improve butanol yield [82–84]. Using starch-based packing peanuts as substrate for continuous production with *C. beijerinckii* BA101strains, 18.9 g/L of butanol could be produced from 80.0 g/L of the substrate within 110 h, indicating the crucial role played by the selection of substrate and microbial strain [85].

C_2, C_3 and *C_4 diols* are highly useful chemical intermediates which can be transformed into a number of value-added products. *Mono ethylene glycol* (MEG) is manufactured by hydrolysis of ethylene oxide, which in turn is produced by catalytic oxidation of ethylene. Major application of MEG is as the monomer in the manufacture of polyester fibre and polyethylene terephthalate (PET), PTA being the other monomer. Other minor applications include anti-freeze and coolants, solvents and chemical intermediates (Fig. 8).

With the growing emphasis on sustainable products, bio-based PET is being manufactured, using bio-MEG produced using ethylene obtained by dehydration of bioethanol. *PlantBottle*, made from PET using bio-MEG and PTA, was introduced by Coca Cola [56, 87] in 2009. Global market for bio-based PET (containing 30% bio-MEG and 70% PTA) is expected to touch 5.8 million tons by 2020 and consequently help in moving towards sustainable packaging applications. Global sustainable packaging market on the same lines is expected to grow from US$ 200.00 billion in 2014 to US$ 267.00 billion in 2020, with a CAGR of 4.9%.

*C_3 diols***,** namely, *1,2 and 1,3 propane diols* are valuable monomers for the production of polyesters, polycarbonates and polyurethanes, besides having applications as anti-freezing agents, additive in nutrition products, solvents and component of hydraulic fluids [56]. 1,3-Propane diol (1,3 PDO) on polymerization with terephthalic acid yields commercial polyesters, SORONA® (from DuPont) and CORTERRA® (from Shell), which are used in the manufacture of high-quality carpet and textile fibres. While 1,2-PDO is produced by selective hydrolysis of

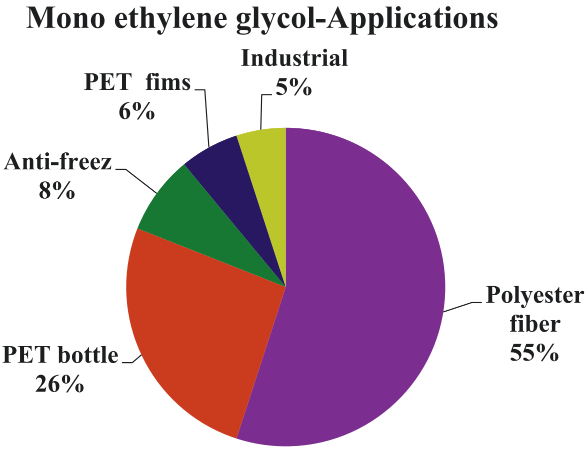


Fig. 8 Applications of mono ethylene glycol [86]

propylene oxide in presence of ion-exchange resin catalysts at 150–180 °C [88, 89], 1,3-PDO is manufactured [90–92] either by Shell process from ethylene oxide or acrolein by DuPont process. Several microbial processes for the production of both 1,2- and 1,3-propane diols [56] using a variety of microorganisms and feedstocks (glucose, glycerol, sugars) have been reported. Notable amongst them is DuPont/Tate & Lyle process [93], in which two conversions, glucose to glycerol by recombinant *E. coli* and conversion of glycerol to 1,3-PDO by *Klebsiella* strains, are combined. The process was first commercialized in 2006, and the capacity was expanded to 65,000 MTA. Similarly, microbial process for the conversion of glycerol to 1,2-PDO using *E. coli* [94] as the microorganism was developed.

Emergence of biomass conversion processes to fuels and chemicals and the large-scale availability of biodiesel-derived *glycerol* as an important platform molecule paved way for the development of sustainable processes for the production of a number of important chemicals and chemical intermediates from glycerol [91, 95–97].

Catalytic processes for the hydrogenolysis of glycerol to yield selectively either 1,2- or 1,3-PDOs have been reported [98–102]. Nakagawa and Tomishige [98] investigated hydrogenolysis of glycerol on four different types of catalysts, namely, non-noble metal catalysts, noble metal catalysts with an acid as an additive, noble metal catalysts combined with a base and metal oxide-modified noble metal catalysts, and observed that only metal oxide-modified noble metal catalysts were selective for 1,3-PDO while the other three catalysts displayed high selectivity for 1,2-PDO. Accordingly, Arundhathi et al. [100] observed that hydrogenolysis of glycerol on Pt-WO_x/AlOOH yields 1,3-PDO with 66% selectivity. Reaction pathways leading to the formation of 1,2- or 1,3-propane diol have been proposed by Nakagawa and Tomishige [98]. Selection of suitable catalyst and reaction conditions for glycerol hydrogenolysis leads to the formation of 1,2- or 1,3-propanediol (Fig. 9).

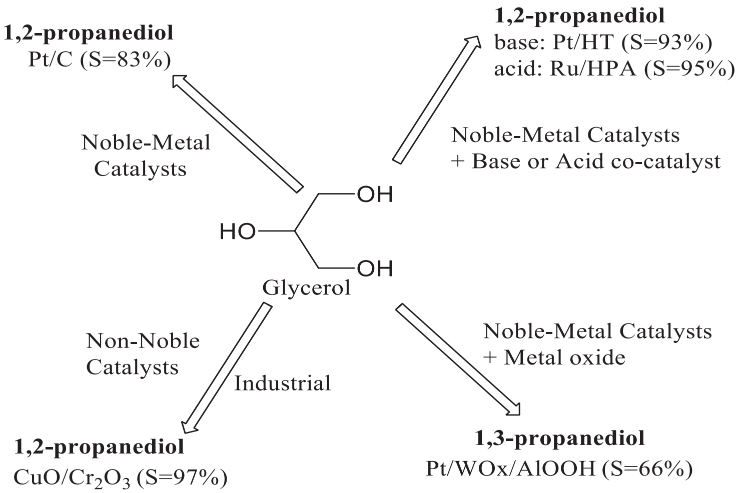


Fig. 9 Selective hydrogenolysis of glycerol to 1,2- and 1,3-propanediols (Adapted from Kuhz et al. [56])

Of the four isomers of *butane diol (BDO)*, 2*,3- and 1,4-BDO* have a wide range of applications, while *1,2- and 1,3-BDO* have relatively limited range of use. While 1,2-BDO is used for the production of polyester resins and plasticizers, the main application of 1,3-BDO is as solvent for food flavouring agents and as co-monomer for some of the polyurethane and polyester resins [103–105].

Amongst the C_4 diols, *2,3-BDO* is perhaps one of the most useful bio-based feedstock chemical intermediates, with applications on several sectors. *2,3-BDO* on dehydration yields 1,3-butadiene, the monomer for synthetic rubber production or methyl ethyl ketone (MEK), useful as solvent and fuel additive. 2,3-BDO itself can serve as an "octane booster" for gasoline and, due to its lower freezing point (−60 °C), anti-freeze agent as well. Diacetyl, a highly valued flavouring agent that protects against bacterial attack, is made by dehydrogenation of 2,3-BDO [106]. Esters of 2,3-BDO and maleic acid are used for polyurethane/maleimide with cardiovascular applications [107]. 2,3-BDO esters are also useful for pharmaceuticals and cosmetics applications. Though 2,3-BDO is produced by chemo-catalytic route via butene-chlorohydrin pathway [56, 108], manufacturing by biotechnological routes using renewable biomass feedstocks and biomass wastes has recently become prominent. Several reviews covering significant developments in the microbial production of 2,3-BDO have been published [109–112]. 1,4-BDO is produced through Reppe chemistry by reaction between acetylene and formaldehyde to form 1,4-butyene diol, which is subsequently hydrogenated to yield 1,4-BDO. Hydroformylation of propylene, hydrogenation of maleic anhydride and dichloro-butene process from 1,3-butadiene or the 1,3-butadiene-acetic acid are the other processes for the manufacture of 1,4-BDO [109, 113]. With the identification of succinic acid as one of the platform chemicals from the biomass refinery, synthesis of 1,4-BDO by reduction of succinic acid as a sustainable process has gained prominence. Microbial routes for 1,4-BDO using engineered *E. coli* microorganisms have been developed up to demonstration scale [114–116]. Major applications of 1,4-BDO include synthesis of gamma butyrolactone, use as solvents and in the manufacture of plastics, fibres and polyurethanes.

C4 and C5 alcohols and diols are highly valuable chemical intermediates used as monomers in the production of polyesters, polyurethanes and polyethers, as fuel additives to boost gasoline octane number and as versatile solvents for various applications. Several process options for the synthesis of *C_{5+} alcohols/higher alcohols/fatty alcohols* are available. Some of the processes developed earlier include [56, 117]:

- Hydrogenation of fatty acids and fatty acid esters derived from vegetable and animal fats and oils.
- Conversion of ethylene with Al alkyls, $Al(CH_2CH_3)_3$ to a mixture of linear, primary alcohols (Ziegler process).
- Hydroformylation of olefins with CO and H_2 to a mixture of branched and unbranched aldehydes and subsequent hydrogenation to the corresponding alcohols.
- Oxidation of paraffins with boric acid to linear, secondary alcohols.
- Condensation of primary alcohols C_2–C_4 with basic catalysts to α-branched and linear, dimeric alcohols based on Guerbet chemistry [118].

Of recent, advances in the development of biomass conversion processes have brought into focus more process options:

- Oligomerization of ethylene derived from bioethanol and bio-methanol conversion through MTO to higher carbon number olefins followed by oxo synthesis and hydrogenation [119–121].
- Condensation of biomass-derived methanol and ethanol to higher alcohols via Guerbet chemistry [118, 122], self-condensation and cross-condensation reactions.

Biomass-derived platform chemicals/intermediates have been used as raw materials for the sustainable production of C_4–C_5 alcohols and diols. A comprehensive review by Sun et al. [123] describes in detail the processes and catalysts developed and other features for the synthesis of C_4–C_5 alcohols and diols from various biomass-based raw materials, like succinic acid, dialkyl succinates, γ-butyrolactone, levulinic acid and alkyl levulinates, γ-valerolactone and furfural and its derivatives.

Since many years, *syngas* has been another rich source for the production of higher alcohols and versatile in application, since it can be obtained from different raw materials, both fossil and biomass based, with several syngas conversion options therein. An extensive review, by Luk et al. [124], covering various process options for the conversion of syngas to higher alcohols, the catalysts and structure-activity correlations therein and the process features, (Fig. 10) along with the details on the applications of C_6–C_{22} long-chain alcohols [125] as feedstocks and chemical intermediates and in polymers, surfactants and detergent industries, has been published.

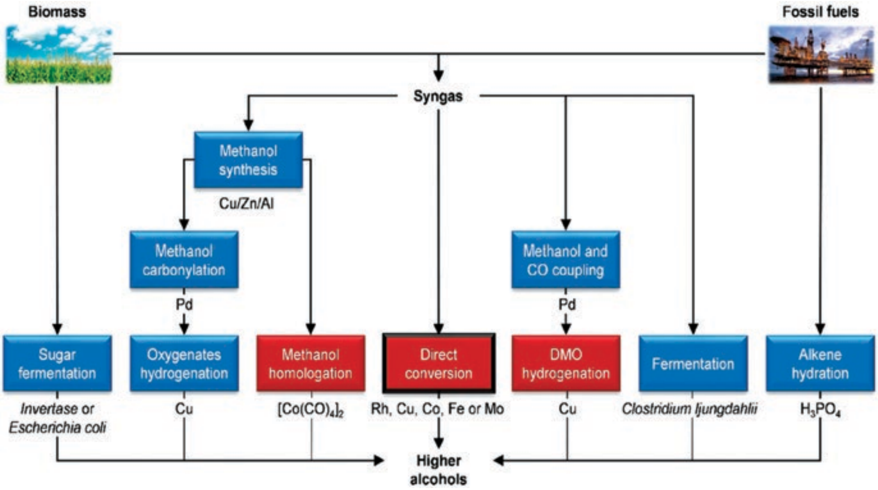
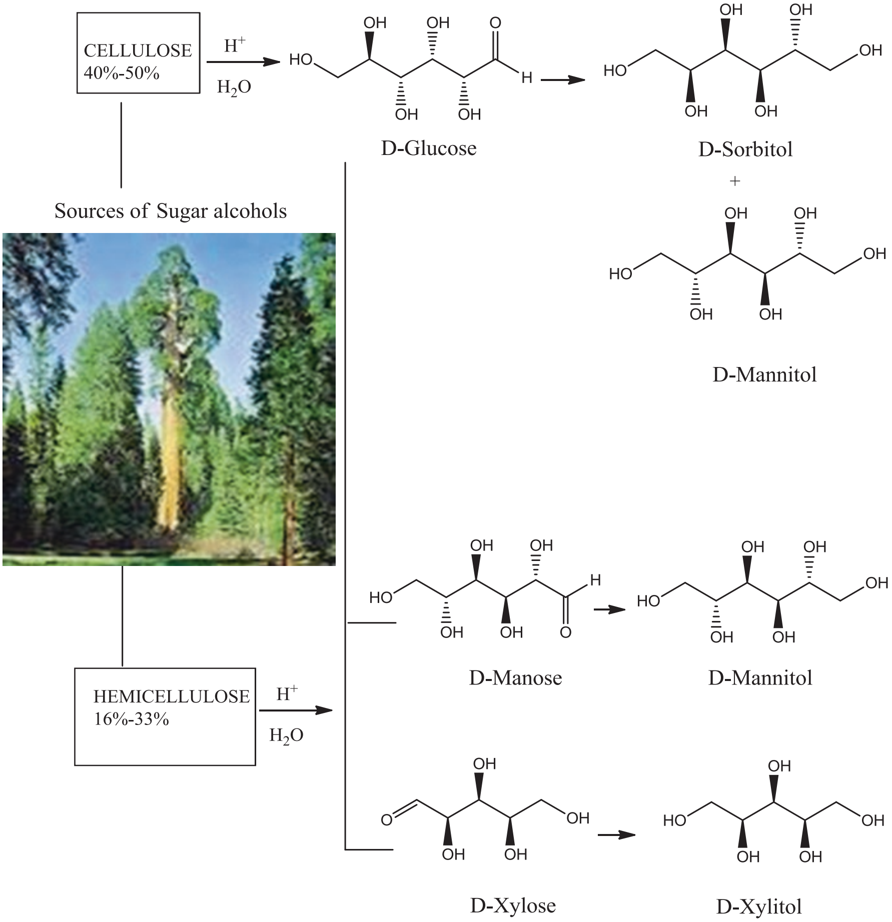


Fig. 10 Syngas conversion to higher alcohols—Process options (Reproduced from Luk et al. [124])

While the classical routes for higher alcohols like direct conversion of syngas and indirect routes like methanol homologation, methanol-CO coupling and methanol carbonylation are still relevant (Fig. 10), several novel routes like alkene hydration, sugar fermentation [126, 127] and, more recently, direct syngas fermentation are emerging as viable and more efficient routes with low carbon footprint. Diender et al. have reported [128] production of C_4–C_6 fatty acids and alcohols from a mixture of syngas and CO, using co-culture consisting of *Clostridium autoethanogenum* and *Clostridium kluyveri*.

Sugar alcohols/polyols/polyhydric alcohols, with the general formula $H_2(CH_2O)_{n+1}$, are well-known biomass-derived chemicals with widespread applications as chemical intermediates and platform chemicals (sorbitol, xylitol and arabinitol) [20, 21]. Mannitol and erythritol are the other two important sugar alcohols [56]. Besides their main use as artificial sweeteners in food, beverages and confectionary, sugar alcohols find applications in polymers, pharma and cosmetics industries [22]. Global consumption of sugar alcohols is projected to grow from 1.6 million metric tons in 2017 to 1.9 million metric tons by 2022 at a CAGR of 3.4% [56, 129]. Sugar alcohols are produced, in general, through hydrogenation or fermentation of mono- or disaccharides [130–132]. While sorbitol and mannitol are synthesized by hydrogenation of sucrose, glucose and fructose [131], xylitol can be produced by hydrogenation of xylose and erythritol by fermentation of glucose [22, 133–135]. Cellulose and hemicellulose, the two major components in biomass, are hydrolysed to glucose, mannose and xylose, which undergo further hydrogenation to yield sugar alcohols as shown in Scheme 1. An extensive review of the catalytic processes for the conversion of glucose, mannose and xylose to sorbitol, mannitol and xylitol, respectively, has been presented by Zada et al. [136]. Detailed studies



Scheme 1 Conversion of cellulosic biomass into sugar alcohols (Reproduced from Zada et al. [136])

on a number of noble metal, non-noble metal and bimetallic catalysts on various supports, along with the activity, selectivity and yield data, have been covered in the review. Different types of catalysts for the production of sugar alcohols by hydrogenation and hydrogenolysis of mono- and disaccharides have been described in another review by Ruppert et al. [92]. Erythritol, a C_4 sugar alcohol, is obtained from pentose sugars (xylose and arabinose) by selective cleavage of C-C bond. Several homogeneous and heterogeneous catalysts have been explored [136] for this process which requires mild reaction conditions (<180 °C temperature and <60 bar hydrogen pressure) to minimize side reactions and achieve selective C-C bond cleavage to yield erythritol [137, 138]. Several microbial processes for the production of sugar alcohols have been described in a review by Kunz et al. [56].

4 Value-Added Products from Alcohols

Abundant availability of nearly complete range alcohols, at low cost, derived mostly from renewable biomass resources, has provided a great impetus for the development of a number of catalytic processes for their conversion into value-added products. Processes for the manufacture of whole range of chemicals that include building block chemicals (olefins and aromatics), oxygenates (aldehydes, ketones, acids, ethers, esters, amides) and fuels (gasoline, diesel, jet fuel and fuel additives) with alcohols as feedstocks have been explored, thus making them as the most versatile group of platform molecules. Salient features of such processes and advances therein are described in the following pages. However, well-established applications of alcohols like conversion of methanol to formaldehyde, acetic acid and MTBE are not covered.

4.1 Conversion of Methanol to C_2–C_3 Olefins

Global demand for ethylene and propylene is estimated as 152 MMT (million metric tons) and 102 MMT, respectively, in 2017 and is projected to reach 185 MMT and 127 MMT by 2022 [139]. Building block olefins like ethylene and propylene along with 1,3-butadiene and butenes (1-, 2- and iso-) are the raw materials for commodity petrochemicals and polymers, and the current dominant route for manufacturing is by highly energy-intensive thermal steam cracking (SC), using non-renewable fossil-based raw materials, ethane/propane or naphtha.

Methanol to olefins (MTO) process developed by UOP-Hydro [140] provided the first commercially viable alternative route for SC process. Based on the tailor-made SAPO-34 catalyst [141–143], the process operates in the temperature range 340–540 °C at 0.1–0.3 MPa pressure, in a fluidized bed reactor (Fig. 11) coupled with catalyst regenerator, considering the deactivation characteristics of the catalyst [144]. Appropriate pore size (3.8 Å), to minimize the formation of higher carbon number products, and optimized acidity, to control the formation of paraffins by hydride transfer, are the key catalyst characteristics responsible for 75–80% carbon-based combined selectivity towards ethylene and propylene. By varying the process conditions, maximization of ethylene or propylene yield could be achieved. Besides ethylene and propylene, small amounts of C_4–C_{6+} olefins are generated. In the advanced version of the process, Olefins Cracking (OC) process technology, developed by Total Petrochemicals [145], which involves routing the by-product C_4–C_{6+} olefins stream through a catalyst bed for further cracking to ethylene and propylene, was integrated with MTO process. This additional process step increases the overall yield of ethylene and propylene and reduces by-products' formation.

With further modifications in the catalyst formulation to maximize propylene, propylene/ethylene ratio >2 (Fig. 12) could be achieved [146]. Similar MTO processes, D-MTO and D-MTO-II (from Dalian Institute of Chemical Physics, DICP,

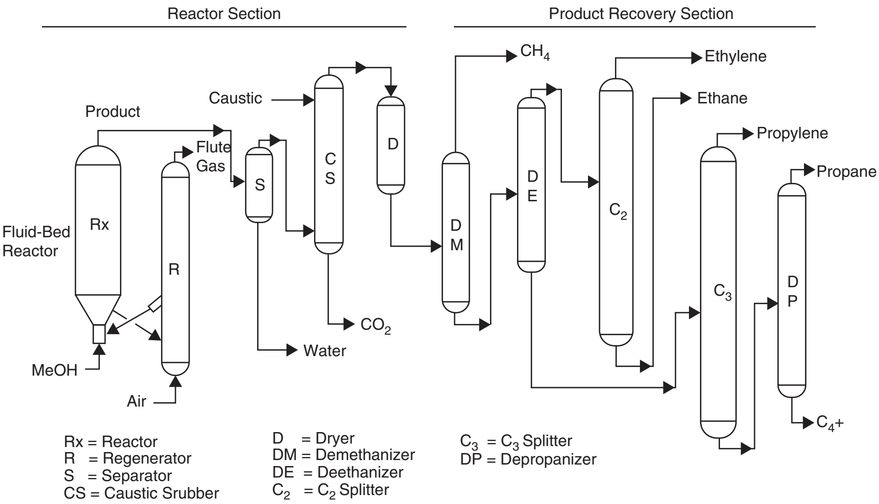


Fig. 11 Simplified process flow diagram for UOP-Hydro MTO process (Reproduced from Keil [144])

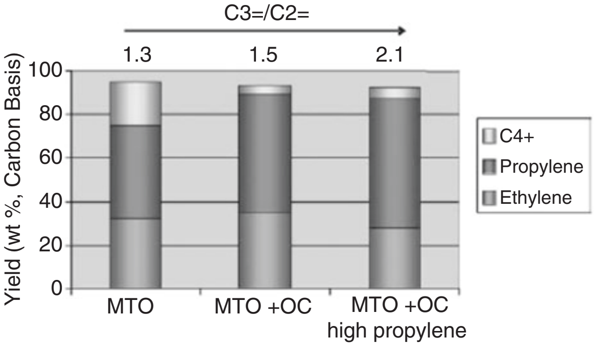


Fig. 12 Increase in propylene/ethylene ratio by integration with OC technology and catalyst optimized for high propylene (Reproduced from Chen et al. [146])

China) and S-MTO (from SINOPEC, China), have been developed and proven on commercial scale [147, 148].

Extensive research work on the mechanism of MTO process under different process conditions (temperature and LHSV) and using C^{13} H_3OH for tracing the reaction pathway by Dahl and Kolboe [149] resulted in the proposal of *hydrocarbon pool mechanism* for the process (Fig. 13).

Comprehensive reviews [147, 148, 150, 151] tracing the first discovery of the MTO process by researchers from Mobil Corporation on ZSM-5 catalysts [152] and the discovery of SAPO-34 catalyst by Union Carbide scientists and further in-depth research work on the catalyst and process development by UOP-Hydro that finally

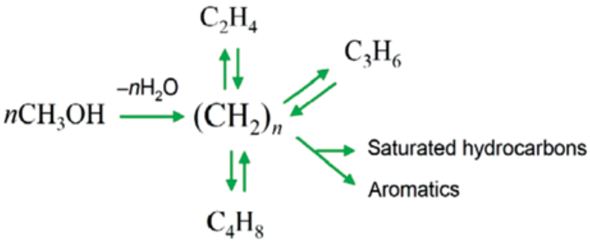


Fig. 13 Hydrocarbon pool mechanism for MTO process. Reproduced from Dahl et al. [149]

lead to the commercialization of the process and the intricacies in the synthesis of SAPO-34 with appropriate structure and topology have been published. MTO process has several advantages in comparison with gas/naphtha steam cracking like:

- Lower reaction temperature.
- Easier separation and purification of products.
- Relatively less capital investment.
- Feedstock flexibility.

Raw material (syngas) for methanol could be obtained from different resources: biomass or coal, waste gases, etc. Since methanol could be obtained from syngas derived from coal gasification, the process is named as CTO (*coal to olefins*), and a commercial plant based on this technology with 0.6 MMTA capacity for ethylene/propylene has been set up by China Shenhua Energy, China [148].

Another process for the conversion of methanol into building block chemicals is the *methanol to propylene (MTP)* process technology developed by Lurgi AG [153].

In the late 1990s, availability of natural gas in plenty led to setting up MegaMethanol plants (5000 MT/day) by Lurgi [154]. With the knowledge base available at that point of time on MTO process using ZSM-5 catalyst [149, 152], Lurgi developed MTP processes to selectively produce propylene, by using suitably modified ZSM-5 catalyst. The process [153, 155] uses a series of adiabatic fixed bed reactors (Fig. 14), wherein methanol is converted to dimethyl ether (DME) at near thermodynamic equilibrium in the pre-reactor. Feed consisting of methanol, DME and water pass through five to six reactors loaded with highly selective and stable ZSM-5 catalyst at 1.3–1.6 bar pressure and 400–450 °C temperature along with recycle olefin stream and steam, to ensure stability of the catalyst. >99% conversion of methanol and DME is achieved with carbon-based propylene selectivity of >70% along with some quantity of gasoline as by-product. After 500–600 h of operation, the catalyst needs regeneration in situ, by controlled coke burning. According to the established material balance, with 1.67 MTA of methanol as feed, 474,000 MT of propylene and 185,000 MT of gasoline could be produced. The first commercial plant using MTP process technology was established in 2011 in China followed by two more plants, and now it is considered as proven technology for on-purpose propylene production [156]. A techno-economic evaluation [157] of MTO vs. MTP has shown that both processes are equally viable, subject to variations in natural

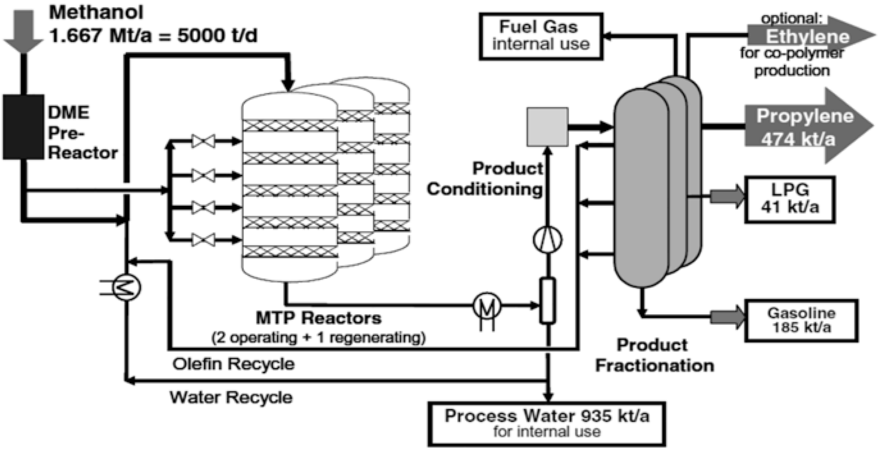


Fig. 14 Process flow diagram for methanol To propylene (MTP) plant (Adopted from Koempel et al. [153])

gas/methanol and products' prices, and MTP has slight advantage in terms of lower CO_2 emission (MT/MT of propylene). Though CTO process may have some advantage due to low-cost coal as raw material, high emission of chemical as well as energy-related CO_2 renders the process environmentally unfriendly [158].

4.2 Conversion of Ethanol to Ethylene

MTO, MTP and CTO processes utilize methanol produced from non-renewable resources. Availability of large quantities of bioethanol at low cost has resulted in the development of catalytic processes for the production of *C_2–C_4 olefins from bioethanol*. Production of *ethylene by catalytic dehydration of ethanol/bioethanol* was established long ago [159, 160], but biomass-derived ethylene as feedstock for petrochemicals was not cost-effective vis-à-vis ethylene from steam cracking [161]. Abundance of bioethanol from different biomass resources (corn, sugar cane and cellulosic biomass) revived the interest in bioethanol conversion to ethylene.

Ethanol dehydration being endothermic in nature (45.7 kJ/mole) requires reaction temperatures in the range 300–500 °C. While acetaldehyde is formed by dehydrogenation at higher temperatures, diethyl ether is formed at temperatures below the optimum. Besides, the product water also influences the reaction. Hence, controlling reaction temperature and maintaining optimum contact time are needed to minimize side reactions.

In practice, isothermal and adiabatic fixed bed and fluidized bed reactors have been considered [163, 164]. Different types of catalysts, like modified alumina, modified HZSM-5, SAPO-34, MCM-41 and modified heteropoly acid catalysts, have been explored, mainly to minimize by-products' formation and improve the

Table 3 Selected catalysts for dehydration of ethanol to ethylene (Adopted from Fan et al. [162])

Catalysts	Ethylene selectivity, %	Ethanol conversion, %	Reaction temp., °C	LHSV[a]/ WHSV[b]/ GHSV[c], h^{-1}	Lifespan, stability
TiO_2 /γ-Al_2O_3	99.4	100	360–500	26–234[a]	400 h, stable
0.5% La-2% P-HZSM-5	99.9	100	240–280	2[b]	Very stable
Nano-CAT	99.7	100	240	1[b]	630 h, very stable
$Ag_3\,PW_{12}O_{40}$	99.2	100	220	6000[c]	Stable in 9% humidity
TPA-MCM-41	99.9	98	300	2.9[b]	Very stable
STA-MCM-41	99.9	99	250	2.9[b]	Stable
TRC-92	99.0	70	280	2.9[b]	Very stable
SynDol (Halcon) (SD, USA)	96.8	99	450	26–234[a]	Very stable

[a] Liquid hourly space velocity (LHSV)
[b] Weight hourly space velocity (WHSV)
[c] Gas hourly space velocity (GHSV)

stability of the catalyst [162]. A list of catalysts that display nearly 100% ethanol conversion with ~99% selectivity for ethylene is presented in Table 3.

Commercial plants, which are in operation for the production of ethylene from bioethanol are America Halcon Scientific Design Inc., USA (with Synthol catalyst, Al_2O_3-MgO/SiO_2); British Petroleum (Hummingbird process, heteropoly acid catalyst); Axens (Atol process); Chematur; Braskem, Brazil; and Dow Chemical [162, 164–166]. Though the processes could be operated with very high efficiency, cost of ethylene from bioethanol is higher in comparison with ethylene from steam cracking (SC) process due to higher cost of bioethanol and very high energy efficiency realized in mega-scale ethylene plants based on SC.

4.3 *Conversion of Bioethanol-Derived Ethylene to C_3, C_4 Olefins*

As illustrated by Hulea [165], well-established olefins conversion processes like dimerization, metathesis, oligomerization, isomerization, cracking and aromatization could be applied for the conversion of bio-based ethylene to value-added products (Fig. 15).

Both homogeneous and heterogeneous catalysts have been studied extensively [167, 168] for the *dimerization of ethylene to 1-butene*, an important co-monomer in the manufacture of commodity polyolefins, like linear low-density polyethylene (LLDPE). Commercial process for the manufacture of 1-butene, the *AlphaButol* technology developed by Axens and SABIC, is based on highly selective (93%)

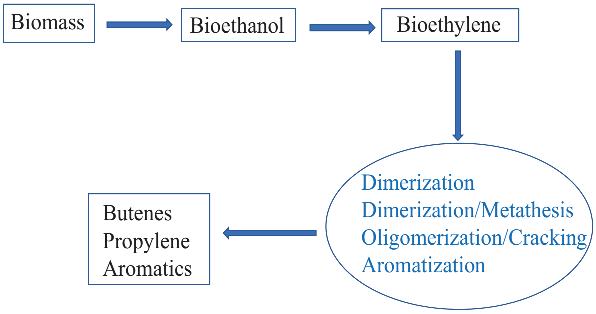


Fig. 15 Process options for the conversion of biobased ethylene to value-added products (Reproduced from Hulea [165])

homogeneous catalyst $Ti(OBu)_4$ with $AlEt_3$ as the co-catalyst. Metal complexes based on Ni, Ti, Zr, Cr, Co and Fe with different co-catalysts in homogeneous medium have been explored for selective *dimerization and oligomerization of ethylene* [168–171]. Such homogeneous catalyst systems, though highly active and selective under mild reaction conditions, require the use of aluminoxane activators or co-catalysts in large amounts and use of solvents/reactants in bulk liquid phase. Besides, many of the metal complexes are not air stable and undergo structural degradation and deactivation, requiring complex regeneration procedures, thus limiting their applications in large-scale continuous mode processes. In order to circumvent such limitations and realize the specific advantages that heterogeneous catalysts offer on these aspects, several types of catalysts in heterogeneous phase, like (a) metal complexes immobilized on polymers and oxides, (b) metal-organic framework (MOF) and covalent organic framework (COF) materials and (c) nickel and palladium supported on inorganic porous materials, have been explored [165]. Nickel metal complexes supported on polymers and inorganic supports like alumina, silica and other zeolites like $AlPO_4$ and Al-MCM-41 display good activity and selectivity for ethylene dimerization, but stability of the active phase during the process and loss of selectivity due to acid-catalysed side reactions on the support that lead to deactivation are the issues. Similarly, metal complexes supported on MOF and COF materials with well-defined chemical environments to promote dimerization and oligomerization are found to be highly active and selective, but the deactivation due to heavier oligomers/polymer formation is the challenge.

In this context, nickel and palladium supported on inorganic porous materials exhibit exceptional performance in ethylene dimerization and oligomerization [168, 172, 173].

Zeolites, sulphated alumina, amorphous silica-alumina and mesostructured MCM-41, MCM-48, SBA-15 and MCM-22 are the supports on which nickel is incorporated by ion exchange as envisaged in the illustration (Fig. 16). Exchangeable Na^+ ions are first exchanged with NH_4^+ ions followed by ion exchange with Ni^{2+} ions and then calcined in air at 550 °C. On thermal treatment, isolated Ni^+ and dehydrated Ni^{2+} species are formed which act as oligomerization sites, and the support provides the acid sites. Such high-temperature treatment ensures thermal stability of the catalyst at temperatures up to 160 °C and pressures up to 40 bar. Besides the reaction could be carried out in liquid phase in slurry mode—gas-solid-liquid – or continuous-flow mode. Mesoporous character of the support leads to facile diffusion of the reactant and products resulting in lower deactivation and higher activity. Besides the chemical nature and acidity, the texture and topology of the mesoporous supports influence the oligomerization activity [174].

For example, Agirrezabal-Telleria and Iglesia [175] observed that Ni-MCM-41 is a very active and selective dimerization catalyst at sub-ambient temperature (243–258 K) with 93% selectivity for 1-butene and TOF > 10 s^{-1} with very little deactivation. The high catalyst activity and stability as well as the C_4 selectivity were attributed to the presence of the ethylene in liquid phase within MCM-41 channels.

Conversion of *ethylene to propylene* is an important process in petrochemical industry considering the supply-demand gap for propylene. Several proven *on-purpose* processes like dehydrogenation of propane, methanol to olefins (MTO) and methanol to propylene (MTP) are available for on-purpose propylene production. Conversion of ethylene to propylene could be achieved through different processes:

1. Metathesis of ethylene and butenes.
2. Direct conversion of ethylene by dimerization and metathesis.
3. Direct conversion of ethylene by oligomerization and cracking.

Metathesis is based on supported Re, W and Mo catalysts, and the process technology is offered by ABB Lummus, BASF and Atofina, Mitsui Chemicals, BP Chemical and Sinopec [176, 177].

Direct conversion of ethylene to propylene actually involves three steps, the first being partial conversion of ethylene to1-butene by dimerization and then isomerization of 1-butene to 2-butene followed by metathesis of remaining ethylene with 2-butenes to yield propylene. Though two-stage processes and single-pot processes have been attempted [165] a cascade process involving two different catalysts is found to be promising (Fig. 17). Andrei and co-workers [178, 179] devised a

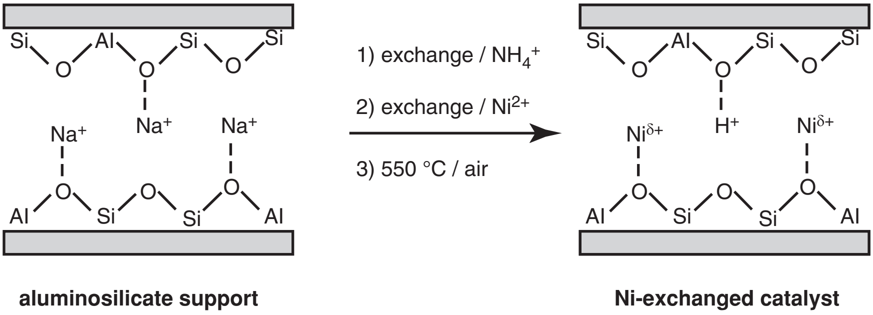


Fig. 16 Ion exchange of Ni^{2+} with the surface Na^{+} ions on zeolite matrix (Reproduced from Hulea [165])

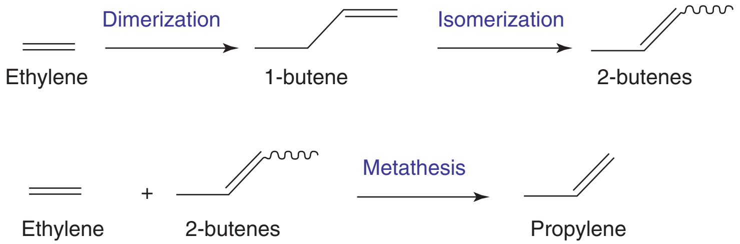


Fig. 17 Cascade process for the conversion of ethylene to propylene (Reproduced from Hulea [165])

cascade process with two different air-stable catalysts, Ni-AlSBA-15 for dimerization and isomerization and MoO_3-SiO_2-Al_2O_3 for metathesis reactions. Both catalysts were loaded in a single reactor, and under identical process conditions, at 80 °C and 30 bar, propylene yield of 48 mmol/g of catalyst per hr. could be realized [178, 179].

For the direct conversion by oligomerization and cracking, ZSM-5 and SAPO-34 were found to be most appropriate [180, 181]. While ZSM-5 with strong acid sites and medium-sized pores (0.55 nm) displayed lower selectivity for propylene, on SAPO-34, with smaller pores (0.38 nm) and weaker acidity, 80% selectivity for propylene could be achieved. The process requires high temperature 450–600 °C to enable the cracking of oligomers. Since the catalysts are acidic in nature and microporous, deactivation by coking is a serious challenge to be tackled.

4.4 *Conversion of Ethanol to C_3–C_4 Olefins*

Two types of catalysts, zeolites and mixed metal oxide catalysts, have been explored for the conversion of ethanol to C_3–C_4 olefins, and the results have been summarized in a review by Sun and Wang [166]. On ZSM-5 reaction follows MTG pathway, involving the formation of ethylene, which undergoes oligomerization, cracking and aromatization to form products with broad carbon number range. Moderation of acidity of ZSM-5 and optimization of reaction temperature and residence time are crucial to minimize the formation of higher carbon number products and improve selectivity towards C_3–C_4 olefins. Studies in this direction by Song et al. [182] on ZSM-5 with different SAR values indicated that selectivity for C_3–C_4 olefins (at 673 K, 0.1 MPa pressure) was maximum (40%) at SAR −80 due to moderation of acidity. On NiO/MCM-41 (Si/Ni = 23) catalyst at 400 °C, complete conversion of ethanol with propylene selectivity of 30% was reported by Mizuno et al. [183]. Reaction pathway involved the formation of ethylene, which undergoes dimerization, isomerization and metathesis to form propylene. Iwamoto et al. [184] observed that on scandium-modified indium oxide catalyst, propylene selectivity of 60% could be achieved at 550 °C following a different reaction pathway, involving condensation and ketonization of acetaldehyde to acetone which is converted to propylene by dehydration of isopropyl alcohol formed by reduction of acetone. Though the metal oxide catalysts display better stability vis-à-vis zeolites, achieving higher C_3–C_4 olefins selectivity remains a challenge.

4.5 Conversion of Ethanol to Isobutene

Two processes, based on mixed metal oxide catalysts, are available for the conversion of ethanol to isobutene [166]. The first one is a two-step process involving formation of acetone from ethanol in the first step followed by its conversion to isobutene in the second step according to the equations:

$$2CH_3CH_2OH + H_2O \rightarrow CH_3COCH_3 + CO_2 + 4H_2 \tag{1}$$

$$3CH_3COCH_3 \rightarrow 2i-C_4H_8 + CO_2 + H_2O \tag{2}$$

The first step involves base-catalysed dehydrogenation of ethanol to yield acetaldehyde, which on aldol condensation and de-carbonylation results in acetone formation [185, 186]. An alternative route [187] consists of oxidation of acetaldehyde to acetic acid, which can undergo ketonization to acetone. Amongst the different catalysts explored [166], Cu supported on $La_2Zr_2O_7$ catalyst [188] displayed 72% carbon selectivity for acetone (96% of theoretical yield) at 400 °C, with water/ethanol mole ratio of 9:1 The second step for the conversion of acetone to isobutene is a complex process, involving three molecules of acetone and many reactions, like condensation, dehydration and decomposition, probably requiring Bronsted or Lewis acid-base pair sites [189, 190], where acetone condensation reaction is initiated. Condensation is envisaged between two acetone molecules, one in gas phase and the other adsorbed on Lewis acid sites, while it occurs through two molecules adsorbed on Bronsted acid sites [191]. Such a complex pathway involving two types of acid sites with varying strengths results in further conversion of isobutene and formation of mesityl oxide intermediates, and higher reaction temperatures lead to formation of aromatics [166]. Zeolite β [192] with moderate acidity displays 87% isobutene selectivity at 400 °C and better stability in comparison with ZSM-5 [193]. Zhu et al. observed that use of nanosize zeolites helps to control the rate of deactivation, possibly by promoting facile diffusion and reducing residence time of reactants and intermediates within the pores [194].

In contrast, the one-step process developed by Zhu et al. [195] uses $Zn_xZr_yO_z$ mixed oxide catalyst with balanced acidity-basicity characteristics. It was observed that addition of ZnO moderated strong acid sites present in ZrO_2, favouring dehydrogenation of ethanol to acetaldehyde against dehydration to ethylene [196, 197]. Aldol condensation of acetaldehyde followed by ketonization leads to the formation of acetone. Presence of weak Bronsted acid sites brings out further conversion of acetone, via diacetone alcohol and mesityl oxide, to the final product isobutene. The process thus follows a cascade reaction pathway, involving dehydrogenation, condensation, dehydration and decomposition reactions, taking place in a sequential manner, yielding isobutene with >80% selectivity in a single step, along with valuable hydrogen as by-product. Overall reaction is expressed as:

$$3CH_3CH_2OH + H_2O \rightarrow i - C_4H_8 + 2CO_2 + 6H_2 \tag{3}$$

While complete conversion of ethanol is achieved, the product distribution and isobutene selectivity are dependent on ethanol concentration and space velocity [197]. Accordingly, maximum isobutene selectivity is achieved at lower ethanol concentration and higher space velocity (Fig. 18), the conditions that help in controlling side reactions.

4.6 *Conversion of Ethanol to 1,3-Butadiene*

Global demand for 1,3-butadiene (BD) was estimated to be ~12.3 MMT in 2018 (Fig. 19) and is projected to touch ~14 MMT by 2025 [198]. Major applications for BD are in the manufacturing of styrene butadiene rubber (SBR), polybutadiene rubber (PBR), acrylonitrile butadiene styrene (ABS), adiponitrile, polychloroprene elastomers, nitrile rubbers and others. Steam cracking of naphtha, dehydrogenation of butane and dehydration of ethanol are the established conventional routes for butadiene production. While the demand for BD is growing steadily, there is some

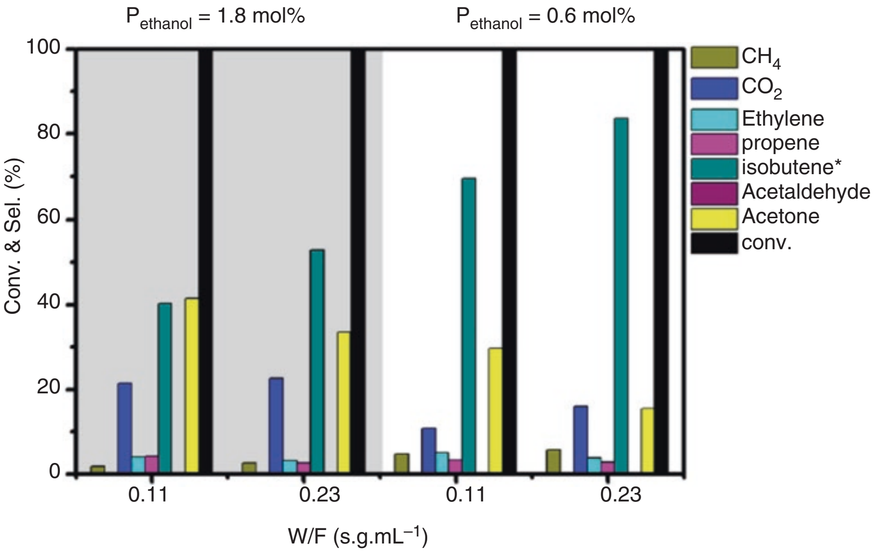


Fig. 18 Conversion of ethanol to isobutene on $Zn_1 Zr_{10}O_x$ mixed oxide catalyst as a function of space velocity and ethanol concentration (Reproduced from Sun et al. [196])

uncertainty in the feedstock scenario, since most of the recent steam crackers are C_2/C_3 gas/shale gas based. Hence, production of BD from readily available low-cost bioethanol and other biomass-derived chemical intermediates has been gaining ground. Accordingly, scientific investigations on catalysts and processes for ethanol to butadiene (ETB) process are on the rise (Fig. 20). A complete life cycle analysis of GHG effect on ETB process vs. naphtha-based one has shown 155% reduction in emissions in the bio-based process [200], thus making it highly relevant in the current context of environmental sustainability of chemical processes.

Historically, two ETB processes have been described. The first one is a single-step process, on ZnO-Al_2O_3 catalyst, at 400 °C, discovered by Sergey Lebedev in 1929 [201–203] according to the reaction:

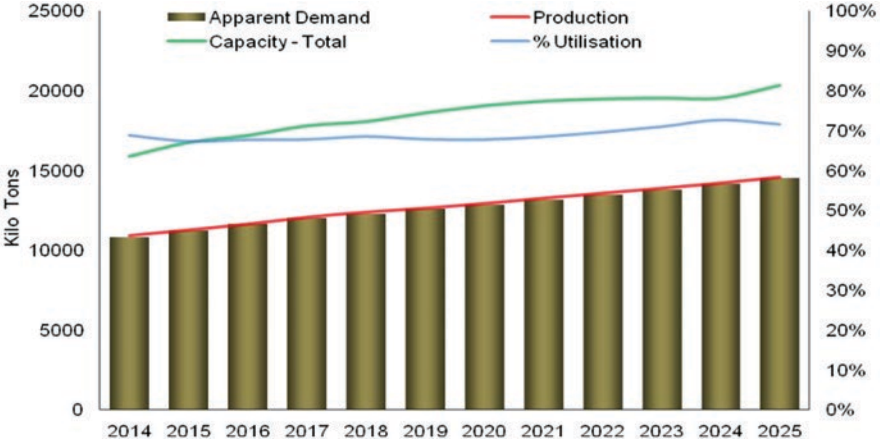


Fig. 19 Global demand/production of 1,3-butadiene [198]

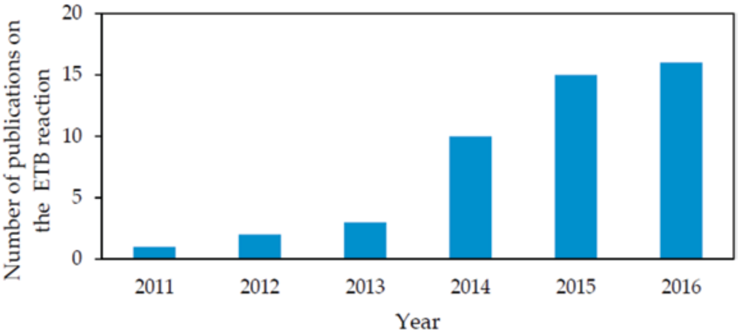


Fig. 20 Number of publications dedicated to ethanol to butadiene in the recent years (Reproduced from Pomalaza et al. [199])

$$2CH_3CH_2OH \rightarrow CH_2 = CH - CH = CH_2 + 2H_2O + \tag{4}$$

and the other, by Ivan Ostromislensky [204], consists of two steps, the first step being partial dehydrogenation of ethanol to acetaldehyde and the second involving reaction between ethanol and acetaldehyde:

$$CH_3CH_2OH \rightarrow +CH_3CHO + H_2 \tag{5}$$

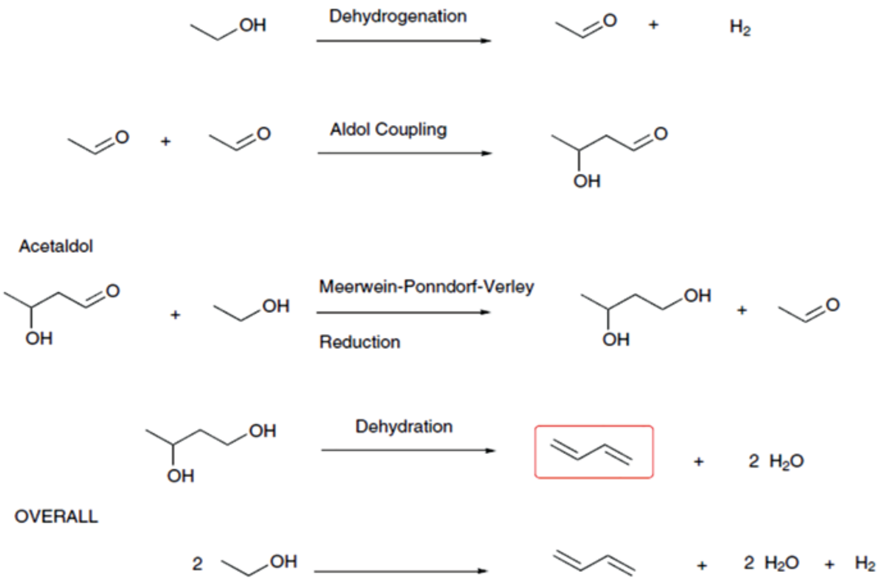
$$CH_3CH_2OH + CH_3CHO \rightarrow CH_2 = CH - CH = CH_2 + 2H_2O \tag{6}$$

Reaction pathways involved in both processes are the same. While Lebedev process [201–203], carried out at 400–450 °C, was based on metal oxide catalysts, Ostromislensky [204] process used tantalum oxide-promoted silica catalyst at 325–350 °C. Commercial production plants based on these processes were in operation till the 1960s, when naphtha-based BD production route became more competitive. Ethanol conversion of 45% with BD selectivity of 55% could be realized in Union Carbide and Chemicals plant [205]. Many by-products, diethyl ether, acetic acid, ethyl acetate, n-butanol, 1-butene, ethylene and hexadiene, were formed in the process. Progress in research related to the different catalyst formulations (mono-, bi- and trimetallic), especially the crucial role of preparation methods, nature of supports, process improvements and understanding of the reaction pathways/mechanism for the conversion of ethanol to BD have been covered extensively in several reviews [199, 206–210].

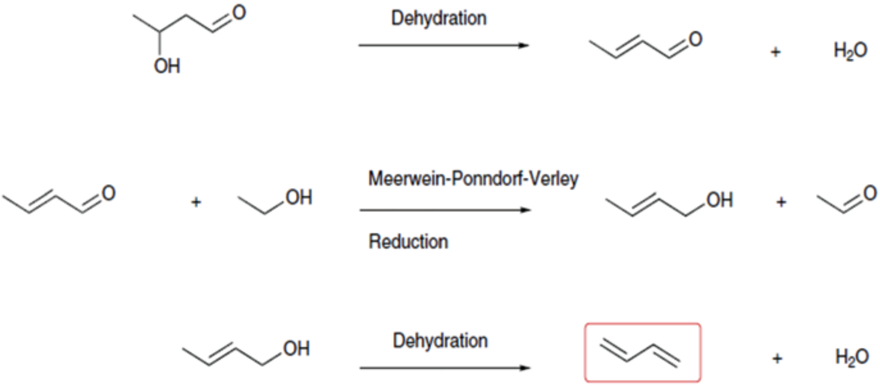
Though different mechanistic pathways have been proposed for ETB process over the years [199, 207], the generally accepted one (Scheme 2) for the single-step process involves dehydrogenation of ethanol to acetaldehyde as the first step, which on aldol condensation yields acetaldol. Meerwein-Ponndorf-Verley (MPV) reduction of acetaldol by another molecule of ethanol gives 1,3-butanediol that subsequently dehydrates to form BD [211, 212]. In the two-step process (Scheme 3), dehydrogenation of ethanol (on copper catalysts) yields acetaldehyde in the first step. In the second step, acetaldehyde forms acetaldol followed by dehydration to crotonaldehyde. MPV reduction of crotonaldehyde by ethanol results in crotyl alcohol, which on dehydration gives BD [213, 214].

Fripiat et al. [215, 216] observed that on silver supported on sepiolite catalyst, selectivity for ethylene and BD increased with ethanol conversion and hence suggested that the process follows Prins reaction pathway. Cavani et al. proposed a different mechanism based on carbanion formation [217]. However, formation of by-products and studies using C^{13}-labelled acetaldehyde supported the mechanism involving MPV reduction [211, 212]. Based on the accepted mechanistic pathway, acidity, basicity and redox characteristics are the functionalities required for conversion of ethanol to BD.

However, developing catalyst formulations that possess the right combination of the active components in required proportions remains a challenge. Details on the development of different types of catalysts for single- and two-step ETB processes have been reviewed from time to time [199, 207–209]. Based on the voluminous



Scheme 2 Reaction pathway for single-step ETB process (Reproduced from Kagan et al. [211] and Vinogradova et al. [212])



Scheme 3 Reaction pathway for two-step ETB process (Reproduced from Kagan et al. [211] and Vinogradova et al. [212])

literature data [199, 206–210], the catalysts investigated so far could be broadly classified into:

- Mixed metal oxide catalysts based on alumina.
- $MgO + SiO_2$ mixed oxides.
- Metal oxide (Cr_2O_3, ZnO, Ta_2O_5, NiO, CuO) and metal (Ag, Au)-promoted $MgO + SiO_2$.

Table 4 Selected catalyst systems for ETB process

Catalyst systems	Reaction temp., °C	BD yield, %	References
$MgO/SiO_2/Cr_2O_3$ (3/2/0.11)	415	41.9	[218]
$MgO/SiO_2/Cr_2O_3$ (59/39/2)	425	39.0	[219]
Mg/sepiolites	300	33.4	[220]
$NiO/MgO/SiO_2$ (10/27.9/62.1)	280	53.0	[221]
MgO/SiO_2(1/1)	350	42.0	[222]
MgO/SiO_2(1/1) + 0.1% K_2O	350	70.0	[222]
MgO/SiO_2(1/1) + 0.1% Na_2O	350	87.0	[222]
MgO/SiO_2 (0.83/1)	350	16.0	[223]
Zr (1.5%), Zn(0.5%)/SiO_2	375	11.5	[210]
Cu (1%), Zr(1.5%), Zn (0.5%)/SiO_2	375	30.1	[210]
5% CuO-MgO/SiO_2 (2/1)	350	58.2	[224]
5% ZnO-MgO/SiO_2 (2/1)	350	52.4	[224]
5% Ag-MgO/SiO_2 (2/1)	350	56.3	[224]
$ZnO.Al_2O_3$ (60:40) fixed bed	425	55.8	[225]
$ZnO•Al_2O_3$ (60:40) fluidized bed	425	72.8	[226]

- Silica-based bimetallic Zr-Zn and trimetallic Zr-Zn-CuO.
- Sepiolite and zeolite (BEA, Al-MCM-41) based.

Table 4 gives a list of selected catalyst compositions and BD yields from the literature [208]. Besides the variations in composition, methods of preparation (wet kneading, sol-gel, hydrothermal), calcination/activation of the catalysts and pore size of the supports are known to influence the activity and selectivity [210, 227, 228]. Though BD selectivity of 50–80% could be achieved, corresponding alcohol conversion levels are lower, and hence there is a need to develop catalysts capable of performing at high ethanol concentrations to obtain higher BD productivity. Current volume productivity of BD in the range from 50 to 400 g BD per hour per litre catalyst volume needs to be improved for commercial application. On-stream stability of the catalyst/catalyst life also needs improvements. Besides fixed bed reactors, other reactor configurations like fluidized bed reactors and the intricacies involved in recycling unreacted ethanol, etc. are to be explored.

A comparative evaluation of naphtha-based and bioethanol-based processes for BD production has been made by Patel et al. [229] in 2012, based on the descriptors for techno-economic viability, sustainability index and life cycle analysis. The descriptors used are economic constraints, environmental impact of raw materials, process costs and environmental aspects, EHS (Environment Health and safety) hazards and risk aspects. After assigning the weightage for each parameter, the integrated score for both processes is presented in Fig. 21. Overall score for bioethanol-based process is lower (0.81), and hence it has a slight edge over naphtha-based (0.9) process. Processing costs and EHS hazards are lower with bio-based process, while risk aspects and environmental impact of raw materials are nearly equal. Economic constraints are higher with bio-based process. However, GHG emission, in terms of kg of CO_2 per kg of BD, is 2.45 for bioethanol-based process vs. 3.98 for

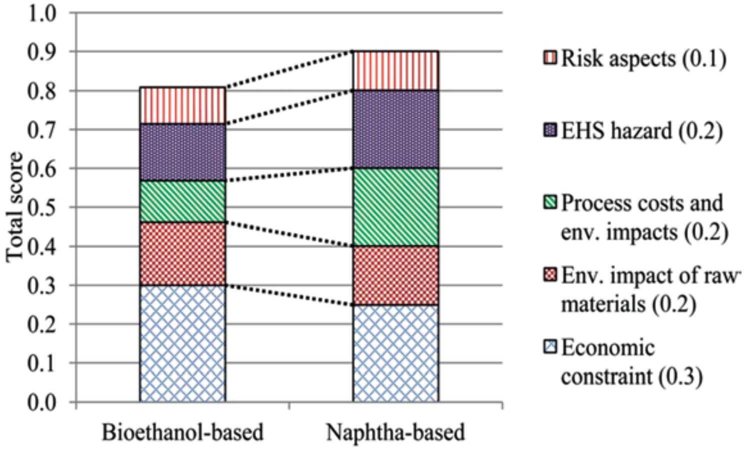


Fig. 21 Comparative evaluation of naphtha-based and bioethanol-based processes (Reproduced from Patel et al. [229])

naphtha-based. Similar advantage in sustainability for bio-based BD process in terms of GHG emissions has been reported by Shylesh et al. [200] in 2016.

Techno-economic analysis of the two-step process carried out by Burla et al. [205] in 2012, based on the conversions and selectivity values achieved in the old Union Carbide plant, has shown that 200,000 MTA BD plant is viable when ethanol and BD prices are favourable and unprofitable when ethanol price becomes >US$ 3.0 per gallon. There is no doubt that ETB process could be a viable one in near future, due to favourable process economics and sustainability. Hence research efforts, especially towards development of catalysts with higher productivity and stability and process improvements, could gain more attention from the researchers and support from the industry.

4.7 Conversion of Alcohols to Fuels

4.7.1 Alcohols to Gasoline

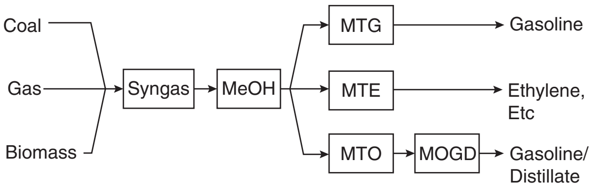
Alcohols, especially methanol and ethanol, find significant applications in the fuel/energy sector, for blending directly with gasoline, as fuel additives/octane-boosting agents, for production of biofuels and biodiesel and, more recently, for conversion into middle distillate range fuels (diesel, jet fuel). Around 31% methanol demand (Fig. 3) is for fuels, for blending with gasoline (13%) and in the manufacture of MTBE (12%), biodiesel (3%) and DME (3%). Utilization of methanol for the production of MTBE and other octane-boosting agents, biodiesel and DME is well-established and understood.

Discovery of *methanol to gasoline* (MTG) on ZSM-5 catalysts in the 1970s by Mobil Corporation opened up a new avenue for direct conversion of methanol [230] to gasoline, to start with. Elucidation of the mechanistic pathways in the MTG process, with methanol and ethanol as feed, by Derouane et al. [231] and Chang et al. [232] and the development of fixed bed reactor process [233, 234] paved way for further improvements in the process. With a better understanding of the catalytic action by ZSM-5 zeolites and the process steps involved, Tabak and Yurchak [235] proposed the integration of MTG process with two other major front-end catalytic processes, namely, methanol synthesis from syngas and syngas production from basic raw materials, coal, gas and biomass. Such a process configuration rendered MTG process more flexible and versatile, capable of producing a range of fuels and chemicals as illustrated in Scheme 4, by suitable optimization of the process conditions. While the use of methanol provided an alternative to route to crude oil-derived gasoline, the pioneering work on ZSM-5 catalysts and demonstration of the other processes (Scheme 4) by Mobil research group [235] for olefins (ethylene, propylene) and middle distillate production provided the scientific basis for the development of several novel and important processes, years later, CTL (Coal to Liquids), GTL (Gas to Liquid) and BTL (Biomass to Liquid) processes, to be followed by MTO and MTP processes. A recent development in this direction is the conversion of ethanol to jet fuels which would be discussed later.

Based on the experience gained in the 14,500 BPD Synfuel MTG plant in New Zealand, CTL process, consisting coal gasification, methanol synthesis plants along with MTG plant with second generation catalyst, [236] was envisaged by Exxon Mobil Research and Engineering (EMRE) and Uhde. The first 2500 BPD CTL plant based on MTG process was established at JAMG, Shanxi Province, China, in 2009 [237]. By 2014, eight such plants were licensed. EMRE-MTG process [238] consists of three units, syngas, methanol and MTG process (Fig. 22), which also includes heavy gasoline treatment unit for removal of durene. Durene with melting point of 79 °C could cause problems in the fuel supply lines and hence is to be minimized to <2% in product gasoline.

Two more processes for MTG have been developed, one by Haldor Topsoe's TIGAS [238] (Haldor Topsoe Improved GASoline) process and the other by Primus STG^{+} [239]. TIGAS mostly resembles EMRE-MTG process except that methanol production unit is integrated with MTG unit and is based on proprietary GSK-10 catalyst for MTG conversion. It is claimed TIGAS process is licensed to three plants in China and two are in planning stage [238].

Improvements in Primus' proprietary STG+™ process [239] over EMRE-MTG and TIGAS processes include recycling unconverted hydrocarbons in a single-loop process so that the gasoline yield increases and up to 70% of natural gas is getting



Scheme 4 Processes for the production of fuels and chemicals from methanol (Reproduced from Tabak et al. [235])

converted directly to high-quality gasoline. Besides, there is no need for separate durene reduction unit. It is further claimed that the Primus process is more energy efficient, requires lower investment cost and amenable for easy scale up.

Sector wise utilization of ethanol (Fig. 23) shows that nearly 50% of the demand is in automobile sector as fuel additive, for blending with gasoline, the other major application being in the food and beverages industry [240]. In contrast to methanol share (Fig. 3) of 64% for chemicals (including 24% for MTO), the usage of ethanol in chemical industry is around ~30%, only, including chemicals, personal care products, pharmaceuticals and others.

Catalytic conversion of *Ethanol to Gasoline* (ETG) has been studied extensively [166], though its large-scale application, like MTG process, is yet to emerge. However, of recent, few processes for conversion of ethanol to diesel and jet fuels

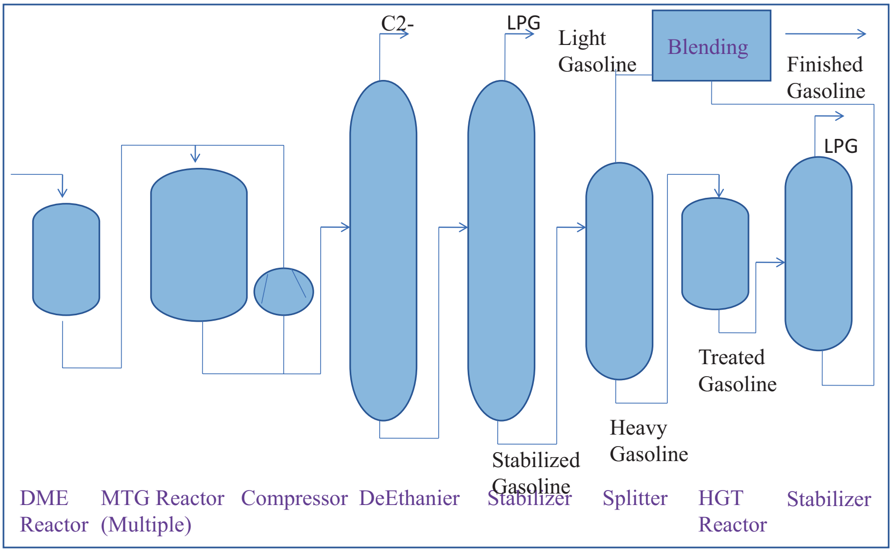
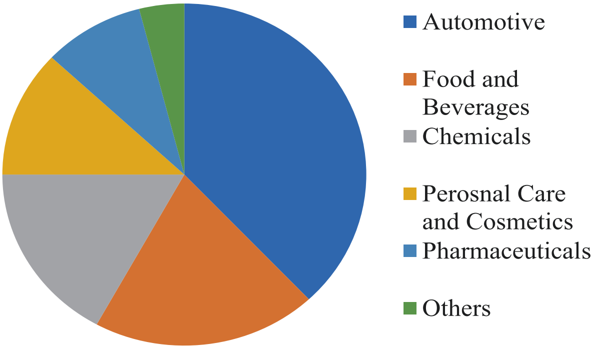


Fig. 22 Simplified process flow diagram for EMRE-MTG process [236]

Fig. 23 Sector-wise utilization of ethanol [240]

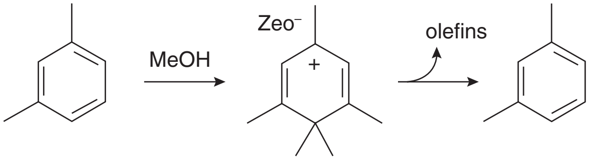


have progressed towards commercial application [241]. ETG process follows nearly the same mechanistic pathway that is proposed for MTG process, and accordingly the product distribution in both cases is similar. Detailed identification and structural analysis of the reaction intermediates trapped inside the pores of ZSM-5 during ETG process have been investigated by Johansson et al. [242]. It is suggested that various types of cyclic organic intermediates (poly-alkylated benzenes) located within the pores form the *hydrocarbon pool* which undergo alkylation-dealkylation and cracking, depending upon the acidity of the zeolite and reaction temperature, thus giving rise to different products.

The transformations occurring in ETG process are similar to those proposed for MTG and illustrated in Scheme 5.

When compared to MTG process, predominantly ethyl-substituted aromatics are found in hydrocarbon pool within the pores in ETG process, but the product stream in ETG, however, contains only methyl-substituted aromatics. Besides, no durenes are observed in ETG [166].

In general, acidity of ZSM-5 as dictated by Si/Al (SAR) ratio, reaction temperature, space velocity and addition of water influence ethanol conversion, product distribution/selectivity and catalyst stability. Major reason for deactivation of ETG catalysts is coke formation, and addition of water retards coke formation and hence less deactivation and improvements in liquid yield [243]. Formation of aromatics/liquid hydrocarbons is favoured with ZSM-5 catalysts with lower SAR [244]. As reported by Talukdar et al. [245], ZSM-5 with SAR-20 yielded full range (olefins and aromatics) products with high liquid yields, while the catalyst with SAR-103 resulted in high yields of light olefins (C_3–C_4) even with ethanol containing 50% water. Investigations by Madeira et al. [246] on ZSM-5 catalysts with SAR values in the range 16–500 have shown that the catalyst with SAR-40 displays the best activity, stability and highest selectivity towards long-chain hydrocarbons and have attributed it to the balance between Bronsted acid sites (active sites) and hydrocarbon radicals (coke species responsible for blocking active sites). Another strategy frequently adopted to moderate acidity and deactivation is by modification/ion exchange with metal ions. Introduction of Ni [247], Ga and Zn [248] ions leads to improvements in catalyst life and increase in liquid hydrocarbon yields. Partial substitution of Al^{3+} in the framework by Fe^{3+} also leads to improvements in liquid yields and stability. Modifications with trimethyl phosphite increase weak acid sites, and accordingly, only ethers appear as products [249]. Besides strong acidity, porosity of ZSM-5 [250] and optimum water content in ethanol [244, 245] are the other parameters that affect the catalyst performance and hydrocarbon yield pattern.



Scheme 5 Representation of hydrocarbon pool mechanism proposed for MTG/ETG processes (Reproduced from Johansson et al. [242])

4.7.2 Ethanol to Jet Fuels and Middle Distillates

Transportation sector accounts for 25% of global total energy demand for the movement of people and goods. The consumption pattern for different types of fuels is given in Fig. 24 [251].

According to International Energy Outlook 2016 [252], the total energy consumption in passenger and freight modes of transportation, using all types of fuels, is increasing (Fig. 25) continuously from ~100 quadrillion Btu in 2012 towards the projected consumption of ~150 quadrillion Btu by 2040 [252]. Considering the need for sustainable energy resources and minimization of the environmental

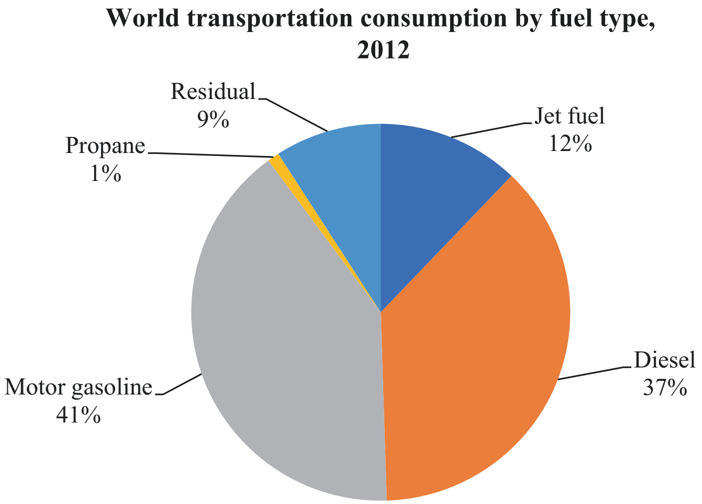


Fig. 24 World fuel consumption for transportation—types of fuels (Total—103 quadrillion Btu) [251]

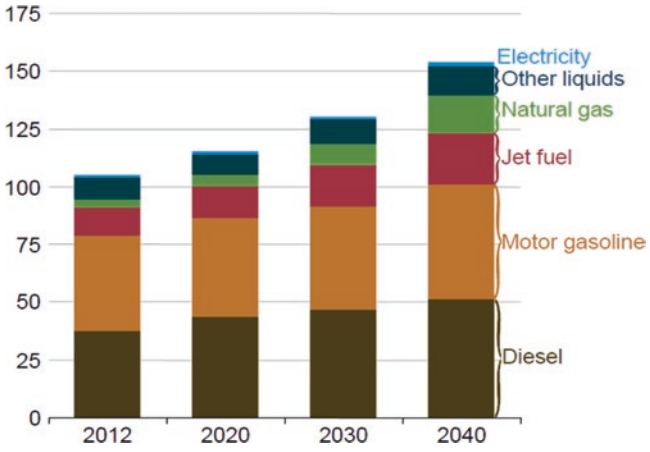


Fig. 25 Global energy consumption in transport sector (in quadrillion Btu) 2012–2040 [252]

impacts, relentless efforts are on to derive these fuels from renewable resources. Significant progress has been achieved in the utilizations of bio-fuels (bio-ethanol, biobutanol, biodiesel, gasoline through MTG process, bio-jet fuels etc.), though overall contribution of bio-fuels in global total energy consumption (in 2017) remains low at 13% [253]. Bio-ethanol, besides its application for blending with gasoline, can be conversted into value-added fuels in middle distillate range and jet fuels by different catalytic processes. Jet fuel constitutes around 12% of the global transportation fuels consumption and its contribution towards emission of greenhouse gases (GHG) is 2%. In order to comply with the Paris Climate Control Accord, 2015, airlines industry is aiming to become carbon-neutral by 2020 and by 2050 reduce emissions by 50% with respect to 2005 emissions level, by gradual replacement of fossil-derived jet fuels with low-carbon bio-based fuels. In this context, besides bioethanol, several process technologies (Table 5) for production of bio-jet fuels have emerged depending on the type of bio-resources used [254]. A number of multinational companies have developed process technologies (Table 6) for the conversion of different types of biomass/renewable feedstocks to bio-jet fuel [255]. While a few of them have gone through ASTM certification process for blending with petroleum-based jet fuel, others are under consideration for certification. Nearly all types of raw materials (Table 6), fossil-based (coal, natural gas), biomass, cellulosic biomass, starch, sugars and bio-renewables like vegetable oils, recycled oil and animal fat have been explored for production of bio-jet fuel. Fermentation, hydrolysis, oligomerization, hydrotreatment and thermal decomposition are the conversion processes employed. Most of the processes listed in the table are in the advanced stage of development, and several airlines have entered into contracts for the supply of bio-jet fuels manufactured by applying these processes [256], for conducting flight trials after mixing with petroleum-derived jet fuel as per ASTM norms.

Compared to the different raw materials used for bio-jet fuels production, bioethanol is better placed with respect to abundant availability and relatively lower cost and hence continues to receive global attention. Recently, a number of SAJF

Table 5 Process technologies for the production of bio-jet fuels (Adapted from Wei-Cheng et al. [254])

Technologies	Production processes
Alcohol to jet (ATJ)	Ethanol to jet
	n-butanol to jet
	Isobutanol to jet
	Methanol to jet
Oil to jet (OTJ)	Hydro-processed renewable jet
	Catalytic hydro-thermolysis
	Hydrotreated depolymerized cellulosic jet
Gas to jet (GTJ)	Fischer-Tropsch synthesis (FT)
	Gas fermentation
Sugar to jet (STJ)	Direct sugar to hydrocarbons (DSHC)
	Catalytic upgrading

Table 6 Bio-based jet fuel production processes—status on development and application [255]

Production process	Developer/manufacturer	Raw materials	Aromatic content	ASTM review stage and max. mixing proportions
FT-SPK	Sasol, Shell, Syntroleum	Coal, natural gas, biomass	Low	(2009)—50% approved
HEFA	Honeywell UOP, Neste Oil, Dynamic Fuels, EERC	Vegetable oil, animal fat, recycled vegetable oil	Low	(2011)—50% approved
SIP	Amyris, Total	Sugar	Low	(2014)—50% approved
ATJ-SPK	Gevo, Cobalt, Honeywell UOP, LanzaTech, Swedish Biofuels, Byogy	Starch, sugar, cellulose-based biomass	Low	(2016)—50% approved
FT-SKA	Sasol	Coal, natural gas, biomass	High	Under review by committee
HDO-SK	Virent	Starch, sugar cellulose-based biomass	Low	Investigation report submitted
HDO-SKA	Virent	Starch, sugar cellulose-based biomass	High	Investigation report under review
HDCJ	Honeywell UOP, Licella, KiOR	Cellulose-based biomass	High	Supplement to investigation report received
CH	Chevron Lummus Global, Applied Research Associates, Blue Sun Energy	Vegetable oil, animal fat, recycled vegetable oil	Low	Investigation report under review

FT-SPK Fischer-Tropsch synthetic paraffinic kerosene, *HEFA* hydrotreated esters and fatty acids, *SIP* synthesized isoparaffins, *SKA* synthetic paraffinic kerosene with high aromatics, *HDO* hydrodeoxygenation, *HRJ* hydrotreated renewable jet

(Sustainable Alternative Jet Fuel) processes using ethanol, methanol, n-butanol and isobutanol have been developed. These processes differ in terms of biomass raw materials used and the processes followed for conversion of biomass to alcohols, types of alcohols and processes adopted for conversion of alcohols to jet fuel. Some of the ATJ/SAJF processes which are in various stages of development are described in the following pages.

Lanza-PNNL Process

LanzaTech Inc. and PNNL (Pacific Northwest National Laboratory) have collaborated to develop a hybrid process, LT-PNNL [257], for the conversion of three different biomass raw materials, wood, corn stover and bagasse, to jet fuel, distillate and value-added chemical, butadiene (BD), following a multistage integrated

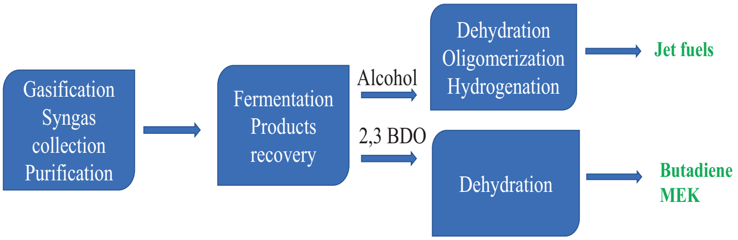


Fig. 26 Block diagram for Lanza-PNNL process for conversion of biomass-derived ethanol to jet fuel and value-added chemicals (Adapted from Ref. [257])

process, as depicted in Fig. 26. The first stage consists of thermochemical conversion of biomass into syngas. The process, that uses highly energy-efficient plasma to convert biomass into clean syngas with consistent composition, was developed by LanzaTech Inc. The process includes collection, compression and purification of syngas. In the second stage, syngas is fed to the bioreactor, wherein it undergoes microbial fermentation process [258] developed by NREL (National Renewable Energy Laboratory), to yield two products, ethanol and 2,3-butanediol (2,3-BDO). The next stage for the conversion of ethanol to jet fuel, involving a series of three catalytic steps, (1) dehydration of ethanol to ethylene, (2) ethylene oligomerization to jet fuel range olefins and (3) olefins hydrogenation, was developed by PNNL [259].

Since direct oligomerization of ethylene is a slow process with lower selectivity/yields towards olefins in the desired carbon number range, a two-stage oligomerization process was developed. In the first stage, ethylene undergoes oligomerization to C_4–C_{10} olefins, which go through further oligomerization in the second stage, to yield jet fuel range olefins [259, 260]. Separation of the fermentation co-product, 2,3-butane diol, and its catalytic conversion to butadiene (BD) were achieved by stepwise catalytic dehydration, first to methyl vinyl carbinol, followed by second dehydration step, to yield 70% BD with 98% purity [257, 261]. Optionally, BDO can be converted to methyl ethyl ketone (MEK). Some of the additional features of the LT-PNNL process are [257]:

- Industrial waste gas streams containing carbon oxides (i.e. steel plant) can be used for ethanol production by fermentation.
- Fermentation process can be optimized for the production of ethanol and BDO in desired proportions, depending on the requirements.
- The process was demonstrated on lab scale with 2000 h of continuous run, producing 400 gallons of jet fuel and 400 gallons of diesel.
- Jet fuel produced meets the specifications designated for “Alcohol to Jet Synthetic Paraffinic Kerosene” (ATJ-SPK) in ASTM D7566, *Standard Specification for Aviation.*

Turbine Fuel Containing Synthesized Hydrocarbons, which specifies requirements for alternative jet fuels

- Co-production of 2,3-BDO/BD reduces overall cost of production.

ORNL-Vertimass Process

Oak Ridge National Laboratory (ORNL) has developed highly versatile process and catalyst [262] for single-step conversion of dilute ethanol from fermentation stream to highly value-added product stream consisting of blend stocks suitable for jet fuel, middle distillate or gasoline. The process is capable of using feedstocks containing 5–100% ethanol in water without external supply of hydrogen and under mild conditions, at low pressure, 60 psi, 350 °C and optimum space velocity (LHSV). Pilot-scale evaluation of the process is to be undertaken by TechnipFMC, and the lab-scale process has been licensed to Vertimass for exploring commercial venture [263–266]. V-, V-In- and Ga-exchanged mono- and bimetallic ZSM-5 catalysts, under optimized process conditions, display C_3–C_{16} hydrocarbon selectivity >80% (Fig. 27) with 100% conversion of ethanol. Light hydrocarbons ($C_2 + C_3$) formation is <5% [267–269]. Metal-exchanged zeolite catalyst in combination with a benzene alkylation catalyst helps to bring down benzene content to <0.68% in the product stream [270], in accordance with environmental regulations.

In order to gain mechanistic insights into the process, studies have been conducted using deuterium-labelled reactants, C_2H_5OD and D_2O and in situ DRIFTS studies [267]. It is observed that with C_2H_5OD as reactant, deuterium is incorporated in product hydrocarbons, but with 70% ethylene and 30% D_2O, deuterium incorporation is not observed. But with 70% ethanol and 30% D_2O, deuterium is incorporated in all hydrocarbons except ethylene. Based on these results and DRIFTS studies, Chaitanya et al. [267] concluded that ethylene is not the intermediate in this process and the reaction proceeds via hydrocarbons pool mechanism.

It is proposed that, unlike LT-PNNL multistep process, which involves ethanol dehydration to ethylene and oligomerization of ethylene to higher carbon number olefins followed by hydrogenation, ONRL-Vertimass process on metal-exchanged zeolite catalysts follows a *consolidated alcohol dehydration-oligomerization* (CADO) pathway to yield, in single step, hydrocarbon blend stocks, suitable for jet

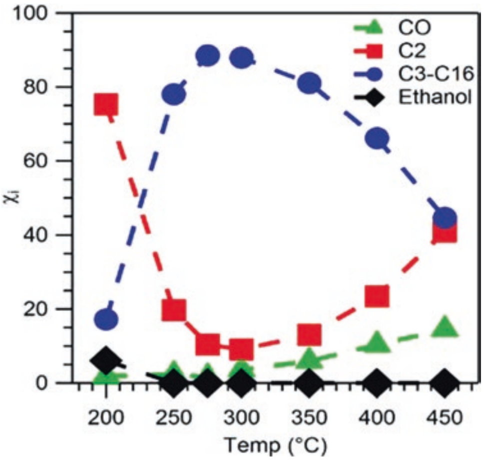


Fig. 27 Ethanol conversion on V-ZSM-5 catalyst as a function of temperature at LHSV-2.93 h^{-1} (Reproduced from Narula et al. [267])

fuel, diesel and gasoline. Product stream composition could be varied depending on market demands by suitable optimization of the process conditions. The lab-scale process has been demonstrated by 200 h continuous run, and the product composition and fuel characteristics have been established. However, long-term stability of the catalyst and ASTM-D-7566 certification are yet to be established. Techno-economic and life cycle analysis [271] of ONRL-Vertimass vs. LT-LNNL processes has shown that the former one is cost-efficient, is viable for blending when oil is at US$100 per barrel and can reduce GHG emissions by 40–96%. Vertimass along with Bioenergy Technology Office of the US Department of Energy would jointly work for further improvements in the process and catalysts and to establish commercial viability.

C_4 Bio-alcohols-Based Processes

Two C_4 bio-alcohol-based processes, one by Gevo, Inc., using bio-isobutanol and the other by *Cobalt Biofuels* (now Cobalt Technologies) using bio-1-butanol, for conversion to jet fuel, have been developed. Sugars extracted from biomass undergo fermentation by Gevo Integrated Fermentation Technology (GIFT) using specific microorganisms to yield isobutanol [272], which is dehydrated to isobutylene. On oligomerization using acidic catalysts like Amberlyst 35, iso-butylene is converted to C_8–C_{16} olefins, which are subsequently hydrogenated to jet fuels [273]. Jet fuel blend from Gevo process has secured certification as per ASTM-D-7566 for blending with commercial aviation fuel. Airliner Delta has entered into an agreement with Gevo, Inc., for offtake of 10 mill gallons per year of bio-jet fuel [274].

CLJ-5 bio-jet fuel developed by *Cobalt Biofuels* is based on 1-butanol obtained by fermentation of C_5–C_6 sugars extracted from cellulosic biomass [275–277]. Bio-1-butene produced by dehydration of bio-1-butanol undergoes oligomerization followed by hydrogenation to yield jet fuels. Oligomerization is achieved by using metallocene catalyst, bis-cyclopentadienyl zirconium dichloride, with MAO as co-catalyst [278]. The process has been demonstrated at pilot scale, and the jet fuel product meets all specifications for blending with JP-5 and other aviation fuels.

Other Processes Based on Ethanol/Alcohols

Conversion of *ethanol to butanol and higher alcohols through Guerbet chemistry* has opened up another route for ethanol to jet fuel (ETJ) production [241], wherein C_4–C_6 alcohols could undergo sequential dehydration, oligomerization and hydrogenation to yield jet fuels. With Cu/MgO-Al_2O_3 catalyst, PNNL [279] could achieve 44% ethanol conversion and 75% C_4+ alcohol selectivity at 300–350 °C and WHSV 0.1–0.2 h^{-1}. However, achieving higher ethanol conversion with high selectivity for C_{4+} alcohols and longer life has been a challenge for ethanol coupling processes. Hence many options for [241] ETJ process are being explored as illustrated in Fig. 28. A combination of two methanol conversion steps, the first through MTO

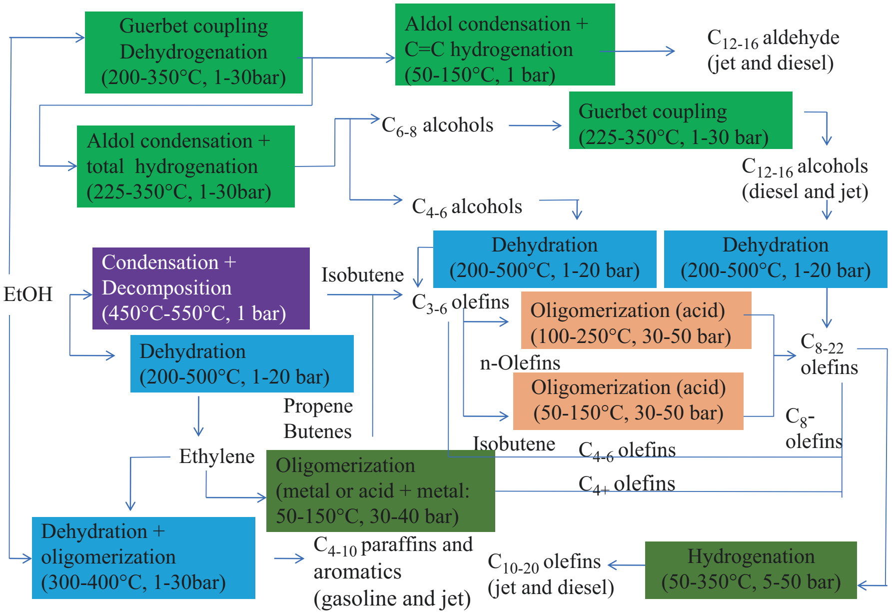


Fig. 28 Various pathways and catalytic processes available for the conversion of ethanol to jet fuel, middle distillates and gasoline (Reproduced from Eagan et al. [241])

(via C_2–C_4 olefins oligomerization and hydrogenation) and the second through DME (via MTG/MOGD), has been envisaged by Bradin [280] for methanol to jet fuel (MTJ) process.

An integrated process involving biomass-derived syngas conversion to a mixture of oxygenates, containing C_1–C_5 alcohols, acetic acid and acetaldehyde, followed by oligomerization and hydrogenation to jet fuel/distillates has been explored by Dagle et al. [281] from PNNL. A systematic review of bio-jet fuel conversion technologies, covering the developments in each case, published by Wang et al. [282], shows that this area has tremendous potential.

5 Aqueous Phase Reforming of Alcohols

Hydrogen is recognized as the clean and efficient source and carrier of energy. Currently, hydrogen is produced by steam reforming, which utilizes non-renewable fossil resources (natural gas, oil, coal) and is highly energy intensive with a large carbon footprint as well. Renewable biomass-based hydrogen production processes like gasification and pyrolysis, though carbon-neutral, are again energy-intensive. In this context, aqueous phase reforming (APR) of biomass feedstocks, developed by Dumesic et al. [283], has emerged as a viable and sustainable route for the production of hydrogen. Unlike steam reforming, APR is carried out at lower temperature (at <500 K compared to 773–1073 K required for vapour phase steam reforming process) and pressure of 20–25 bar, to maintain water in liquid state, thus eliminating energy required for evaporation. Besides, APR includes water-gas shift reaction (WGS) that involves the formation of additional hydrogen to lower CO content, along with the conversion of CO to CO_2 [284].

Aqueous solutions containing 5–20 wt% of any type of biomass intermediates/platform chemicals, like cellulose, C_5–C_6 sugars, polyols and C_1–C_4 aliphatic alcohols, could be used as feed, rendering APR as a highly versatile process for the production of fuels and chemicals from biomass [285, 286]. APR is a carbon-neutral process, which can be integrated with other biological, thermal, chemical or fermentation processes [287] without the need for external hydrogen source. A recent Scopus survey (Fig. 29) brings out a quick indication of the level of global research activity in APR, with all types of biomass feedstocks, in terms of number of publications, in the past two decades.

Transformation of alcohols under APR process conditions is represented by the following reactions/equations:

$$C_nH_{2n+2}O_n + nH_2O \rightarrow nCO_2 + (2n+1)H_2 \tag{7}$$

C-C bond breaking could lead to the formation of CO, which can undergo water-gas shift reaction to yield hydrogen.

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{8}$$

Side reactions involving CO_2 are possible, especially at lower reaction temperatures, leading to the formation of alkanes via methanation and Fischer-Tropsch reactions:

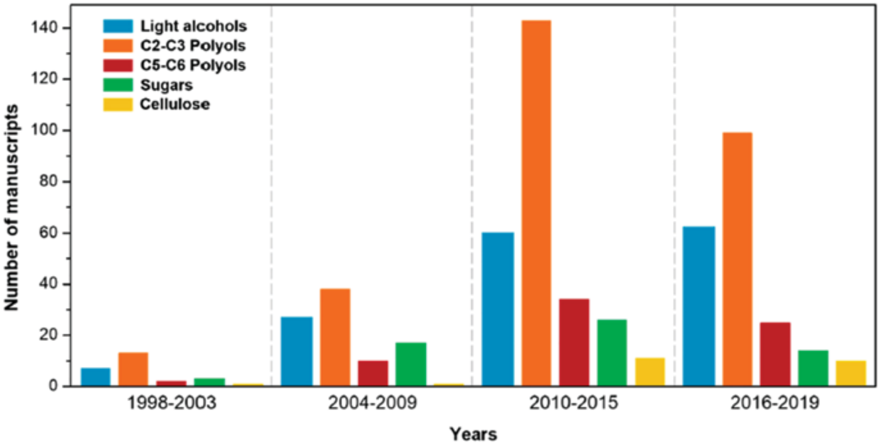


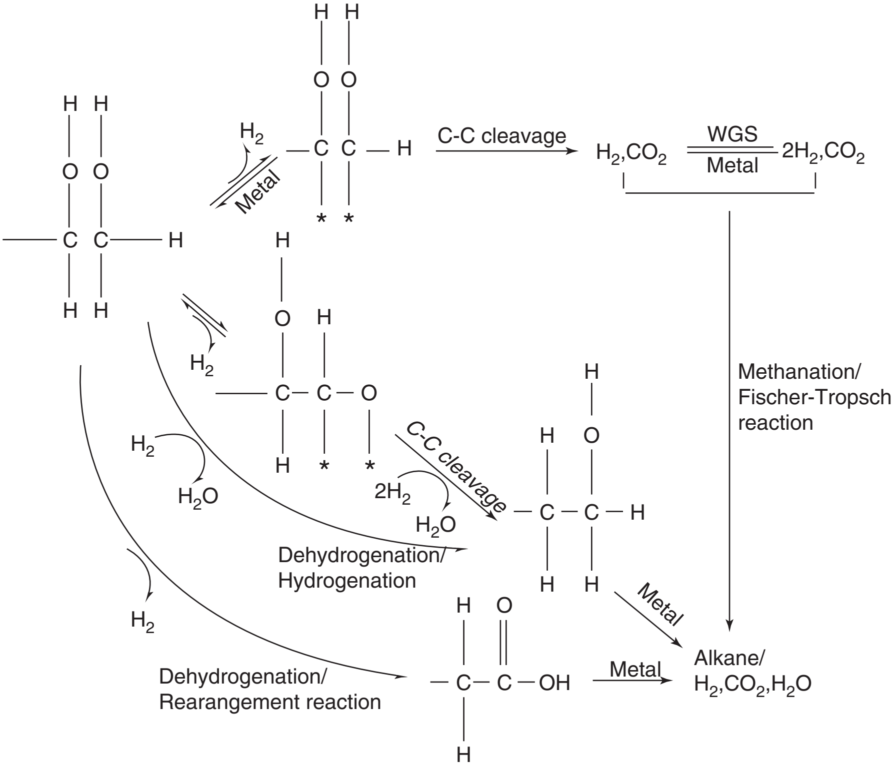
Fig. 29 Trend of the peer- reviewed manuscripts contain "X aqueous phase reforming" (with X = methanol, ethanol, EG, glycerol, sorbitol, etc.) in abstract, keywords and title (Adapted from Scopus® (accessed on Oct 4, 2019) (Reproduced from Fasolini et al. [286]))

$$3H_2 + CO \rightarrow CH_4 + H_2O \tag{9}$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \tag{10}$$

$$nCO + 2nH_2 \rightarrow [—CH_2—]n + nH_2O \tag{11}$$

Mechanistic pathways followed during reforming of alcohols towards the formation of hydrogen and alkanes have been investigated in detail by Davda et al. [288] with *ethylene glycol* as the substrate, as illustrated in Scheme 6. Preferred pathway involves initial dehydrogenation, followed by the C-C bond cleavage of the adsorbed intermediate to yield CO, which undergoes water-gas shift reaction forming hydrogen and CO_2. Cleavage of C-O bond is not desirable since it would lead to the formation of acids. Thus, dehydrogenation and C-C bond cleavage are the two essential catalytic functionalities required for hydrogen production. While supported metal catalysts, in general, are suitable for these surface transformations, side reactions, methanation and F-T synthesis reactions involving the products, CO_2 and H_2, are also possible depending on process conditions. Reforming of two polyols, ethylene



Scheme 6 Reaction pathways during aqueous phase reforming of ethylene glycol (Reproduced from Davda et al. [288])

glycol and glycerol, has been investigated extensively, and comprehensive reviews covering noble (Pt) and non-noble (Ni) monometallic and bimetallic (Pt-Re, Pt-Mn, Pt-Ni and Ni-Sn) catalysts on various supports and the influence of process conditions have been published [287, 289].

In the case of ethylene glycol, the order of activity on silica-supported metal catalysts was observed to be Pt ~ Ni > Ru > Rh > Pd > Ir, with Pt and Pd displaying high selectivity for H_2 formation while Ni and Rh for alkanes [288]. Amongst the supports investigated, alumina, silica, activated carbon (AC), mesoporous carbon (CMK-3) and pseudo-boehmite (Catapal B) for monometallic Pt and bimetallic Pt-Re and Pt-Mn catalysts [290–292], CMK-3 and AC exhibited higher conversion and selectivity for H_2 and better hydrothermal stability compared to silica and alumina supports. Kim et al. [291] have investigated several bimetallic catalysts supported on CMK-3 and observed that Pt-Re displayed high conversion (44.2%) but higher alkane selectivity (19.8%), while Pt-Mn exhibited lower conversion (39.7%) and lower alkane selectivity (2.9%) with higher hydrogen production rate, 26.8 cm^3/g/min vis-à-vis 19.8 cm^3/g/min for Pt-Re catalyst. Higher activity observed with bimetallic Pt-Mn and Pt-Ni catalysts is attributed to alloy formation [291, 293]. According to Bai et al. [294], addition of basic components, MgO and CeO_2, to alumina-supported Pt-Re catalysts resulted in 100% conversion and nearly 100% H_2 selectivity. Increase in Pt dispersion by addition of CeO_2 and moderation of alumina acidity by MgO are proposed to be responsible for high activity and selectivity. Choice of support, tuning support characteristics, metal loading and the active phase composition are thus crucial to achieve higher conversion as well as selectivity.

Similar studies on supported metal catalysts, especially on Pt-based mono- and bimetallic catalysts, on different supports, have been reported for aqueous phase reforming of *glycerol* as well [287, 289]. One significant observation [295, 296] is that larger Pt particles lead to a decrease in H_2 and CO_2 formation and C-C bond cleavage is favoured by small Pt particles as against C-O bond cleavage and hydrogenation reactions, thus highlighting the importance of catalyst preparation methods to achieve higher metal dispersion. Though nickel-based mono- and bimetallic (Pt-Ni) catalysts were active for APR of glycerol, deactivation of catalysts was a major concern, and several strategies, like changes in method of preparation (sol-gel, combustion synthesis), choice of supports and promoter elements, have been adopted to improve the stability of the catalyst [289]. Wen et al. [297] observed that for Pt-based catalysts, basic supports (MgO, CeO_2) resulted in higher conversion and selectivity, while neutral (AC) and acidic supports (alumina, silica, HUSY) increased the formation of alkanes. An exhaustive review by Fasolini et al. [298] covering the catalysts and process features in steam reforming and aqueous phase reforming of glycerol brings out the latest developments on these two processes. Highly efficient catalysts for both glycerol steam reforming (Ni/La_2O_3-Al_2O_3 catalyst with 100% conversion and 99.7% H_2 yield [299]) and aqueous phase reforming (Pt-Ni-Ce/Al_2O_3 catalyst with 96% conversion and 96% yield [300]) have been reported.

Though many methods for reforming of *ethanol* like steam reforming, oxidative reforming and autothermal catalytic reforming are known, all of them involve higher reaction temperatures and tedious hydrogen purification processes due to high CO contents [291, 301].

Tokarev et al. [302] reported nearly complete conversion (98.3%) of 10% ethanol in water, during APR on Pt/Al_2O_3 catalyst at 225 °C and 29.3 bar pressure, in continuous-flow mode and observed hydrogen production of 0.15 mmol/min and stable activity. Addition of 10% sorbitol or 10% glycerol to aqueous ethanol solution resulted in increase of hydrogen production to 0.71 and 0.30 mmol/min, respectively, along with methane and CO formation. In the case of alumina (prepared by solution combustion synthesis—SCS)-supported Ni (10% w/w loading) catalyst for ethanol reforming, Roy et al. [303] observed that surface modification of the catalyst by non-thermal RF plasma treatment resulted in improvement in the ethanol conversion from 81.2% on unmodified catalyst to 85.9% on modified one at 225 °C, which displayed no deactivation for 144 h. Hydrogen yield was also higher, at 381 μmol/min for modified catalyst in comparison with 334 μmol/min for unmodified one. Roy et al. [303] attributed the superior performance of plasma-treated catalyst to an increase in Ni metal dispersion, stronger metal-support interaction and increase in acidity. Detailed studies on the influence of preparation methods for Ni/Al_2O_3 [304, 305] and Ru/TiO_2 [306] catalysts on the performance for ethanol reforming process have also been reported. Nickel supported on Mg-Al hydrotalcites with basic character and higher surface area and pore volume displays higher ethanol reforming activity compared to Ni/Al_2O_3 [307]. Though *n-butanol* has higher hydrogen content (13.5% w/w) compared to ethanol (13%) and methanol (12.5%), n-butanol conversions are low, 5.77% on Ni/CeO_2 and 2.77% on Ni/Al_2O_3 at 488 K [308]. Both noble metal (Pt, Pd) and non-noble metal (Ni) catalysts have been explored for reforming of *sorbitol and xylitol* [289]. Higher hydrogen yield and hydrogen selectivity were observed for xylitol in comparison with sorbitol, since its longer carbon chain leads to higher alkane formation.

Comparative evaluation of the APR activity of different alcohols has been reported albeit with some contradictions. While Shabaker et al. [309] reported similar APR rates for methanol and ethylene glycol on Pt/Al_2O_3, with higher hydrogen production rate for methanol, Liu et al. [310] reported higher ethylene glycol reforming rates with higher hydrogen selectivity compared to methanol, on Pt catalysts on five different supports.

According to Cortright et al. [283], amongst different alcohols, maximum selectivity for hydrogen production was observed with methanol, with lowest CO_2 production, since it has lowest number of carbon atoms (Table 7).

These studies reveal that C-C bond cleavage is not the decisive step in APR process and the reaction mechanism varies with the type and molecular structure of the substrate alcohol.

Table 7 APR reaction data for different alcohols on Pt-based catalysts

Feedstock	Concentration, %	Carbon in liquid/gas phase effluents, %	Hydrogen selectivity, %	Alkane selectivity, %	CO_2 in gas phase effluent, %
Methanol	12.5	6.5/94	99	1.7	25
Ethylene glycol	9.7	11/90	96	4	29
Glycerol	8.6	17/83	75	19	29.7
Sorbitol	7.6	29/61	66	15	35

Temperature, 498 K; pressure, 2.9 MPa (Adapted from Cortright et al. [283])

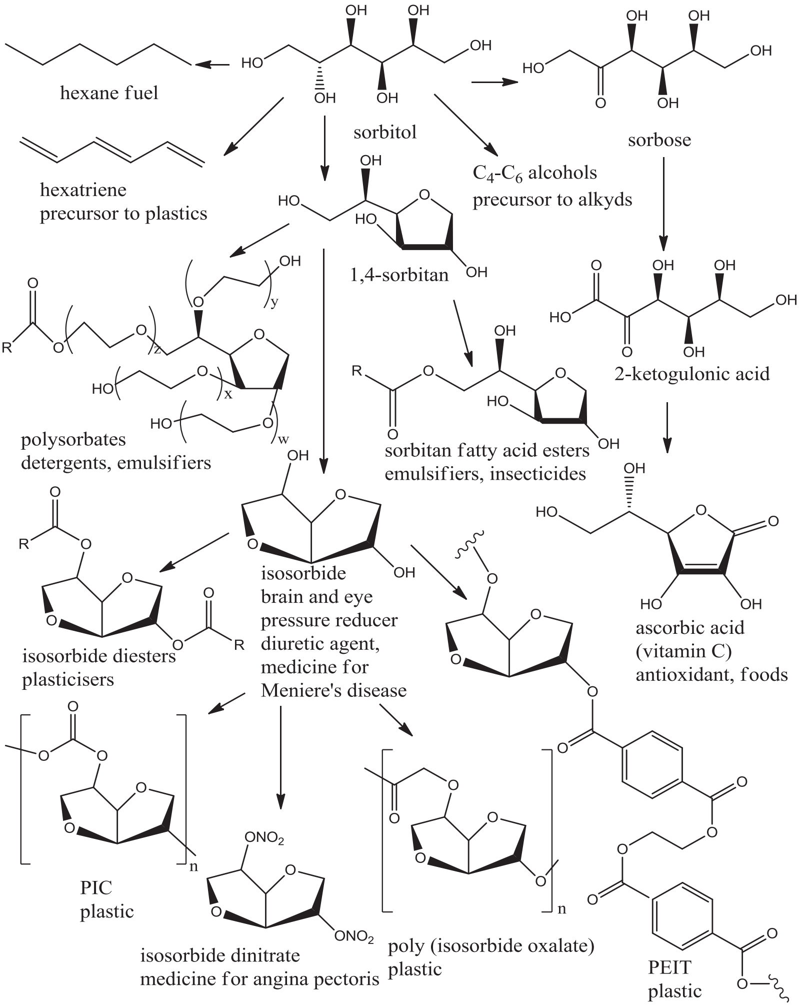
6 Value Added Products from Sugar Alcohols: Sorbitol, Mannitol and Xylitol

Sorbitol is a versatile platform chemical with highly reactive hydroxyl groups, which undergo a variety of transformations like dehydration, hydrogenolysis, oxidation and aqueous phase reforming to yield value-added products with many applications [136, 311]. An illustration of the applications of sorbitol and its derivatives in pharma, medicinal, cosmetics, food, confectionary, bioplastics and elastomers industries, brought out by Kobayashi and Fukuoka [312], is presented in Scheme 7. Isosorbide (1,4:3,6-dianhydrohexitol) is one such derivative of sorbitol, with multiple applications (Scheme 7) with a market size of US$ 396 million in 2018 which is projected to grow at CAGR of 8.5% during 2019–2025 [313]. A number of isosorbide-based biopolymers like polyethylene isosorbide terephthalate (PEIT), polycarbonate, isocyanate-free polyurethane [314], polyisosorbide succinate and isosorbide diesters are produced from isosorbide. Hence, production of isosorbide from sorbitol by acid-catalysed stepwise dehydration (Scheme 8) and directly from cellulose has been the subject of extensive investigations. Different types of solid acid catalysts like supported metal catalysts, zeolites, heteropoly acids, metal phosphates and ion-exchange resins have been explored for the conversion of sorbitol to isosorbide [136, 311]. Otomo et al. [315] could achieve isosorbide selectivity of 80% with zeolite β catalyst with SAR-75. Sulphonic acid-functionalized silica, modified with optimum loading of (3-mercapto-propyl) trimethoxy silane (MPTS) catalysts displayed better performance, with 100% sorbitol conversion and 84% yield of isosorbide [316]. Direct conversion of cellulose to isosorbide, using a combination of Amberlyst 70 ion-exchange catalyst (for cellulose hydrolysis to glucose and dehydration of sorbitol to isosorbide) and 4% Ru/C (for hydrogenation of glucose to sorbitol) to get 55.8% yield of isosorbide in single-pot process, has been reported by Yamaguchi et al. [317].

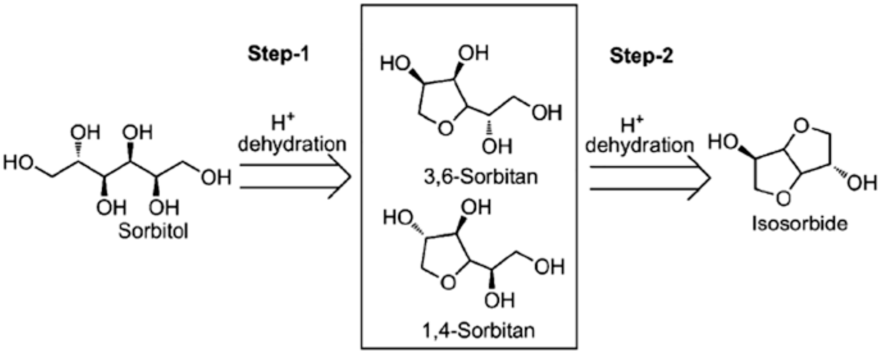
Besides the applications indicated in Scheme 7, catalytic conversion of sorbitol to alkanes via aqueous phase reforming and hydrogenolysis to ethylene glycol and 1,2- and 1,3-propylene glycols are the other important and well-known applications of sorbitol [136, 312].

Mannitol is useful in the synthesis of surfactants, resins and biofuels [318, 319], and mannitol-boric acid complex is used in the preparation of dry electrolytic capacitors. Mannitol has several crucial applications in the field of medicines [136]: (1) as a powerful osmotic diuretic, enhancing the urination to prevent renal failure by removing toxic materials from the body, (2) for reducing the brain swelling, (3) in enhancing the drugs' transport across the blood-brain barrier for the treatment of acute brain diseases and (4) as a common vasodilator for the treatment of hypertension.

Xylitol is yet another platform chemical which is used in food, bakery and confectionary industries. Though not widely used in the chemical industry due to its



Scheme 7 Applications of sorbitol and its derivatives (Reproduced from Kobayashi and Fukuoka [312])



Scheme 8 Stepwise dehydration of sorbitol to isosorbide (Reproduced from Zada et al. [136])

inert nature, it is an active ngredient in several pharmaceutical, dental and oral care products [136].

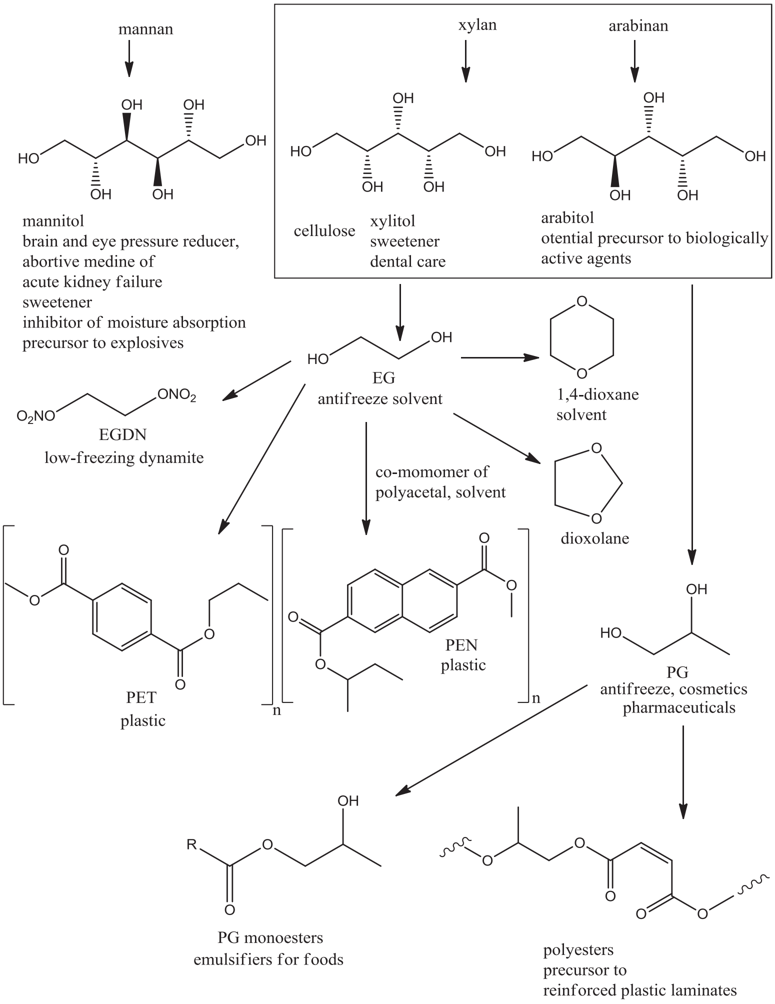
Catalytic conversion of xylitol to value-added products, ethylene glycol and propylene glycol, proceeds through dehydrogenation, retro-aldol condensation and re-hydrogenation pathways [320, 321]. An illustration of the major applications of mannitol, xylitol and arabitol, another sugar alcohol, according to Kobayashi and Fukuoka [312], is presented in Scheme 9.

7 Conversion of Glycerol into Value-Added Products

Applications of glycerol as a versatile platform chemical, capable of undergoing a variety of sustainable chemical transformations towards a wide range of value-added chemicals, fuels and fuel additives, have been reviewed comprehensively [91, 95–99]. Some of the unique features of glycerol that make it as the most useful raw material are:

- Abundance and low cost.
- Utilization as crude glycerol.
- Amenable to chemo- as well as bio-catalytic conversions.
- Highly reactive functional groups.
- Wide spectrum of products based on types of catalysts/reaction conditions.

A summary of value-added products from glycerol (Fig. 30), through different catalytic processes, types of catalysts and developments therein, reported up to 2009, has been published by Bozell and Petersen [21]. Two recent comprehensive reviews by Nda-Umar et al. [322] and Cognet and Aroua [323] on this topic cover the latest developments in the processes, catalysts and other features for the production of many glycerol derivatives indicated in Fig. 30. Non-combustion routes like steam reforming, partial oxidation, autothermal reforming and aqueous phase



Scheme 9 Applications of mannitol, xylitol and arabitol (Reproduced from Kobayashi and Fukuoka [312])

reforming and supercritical water reforming are available for the conversion of *glycerol into hydrogen and syngas* [322]. Both nickel- and platinum-based catalysts supported on modified (especially with ceria) alumina have been explored for steam reforming [322]. 10%Ni/5%CeO_2-Al_2O_3 at 650 °C displayed 85.7% selectivity for hydrogen in continuous-flow packed bed reactor [324]. For APR of glycerol, 71.9% yield of hydrogen could be obtained on 1.44% Pt/Al_2O_3 at 225 °C, pressure = 2.3 MPa time = 3 h, with 100 mg of catalyst [325].

Though glycerol conversion and hydrogen production in APR process are, in general, less in comparison with steam reforming, utilization of crude glycerol in APR is less energy-intensive since vaporization is not required. Hence further

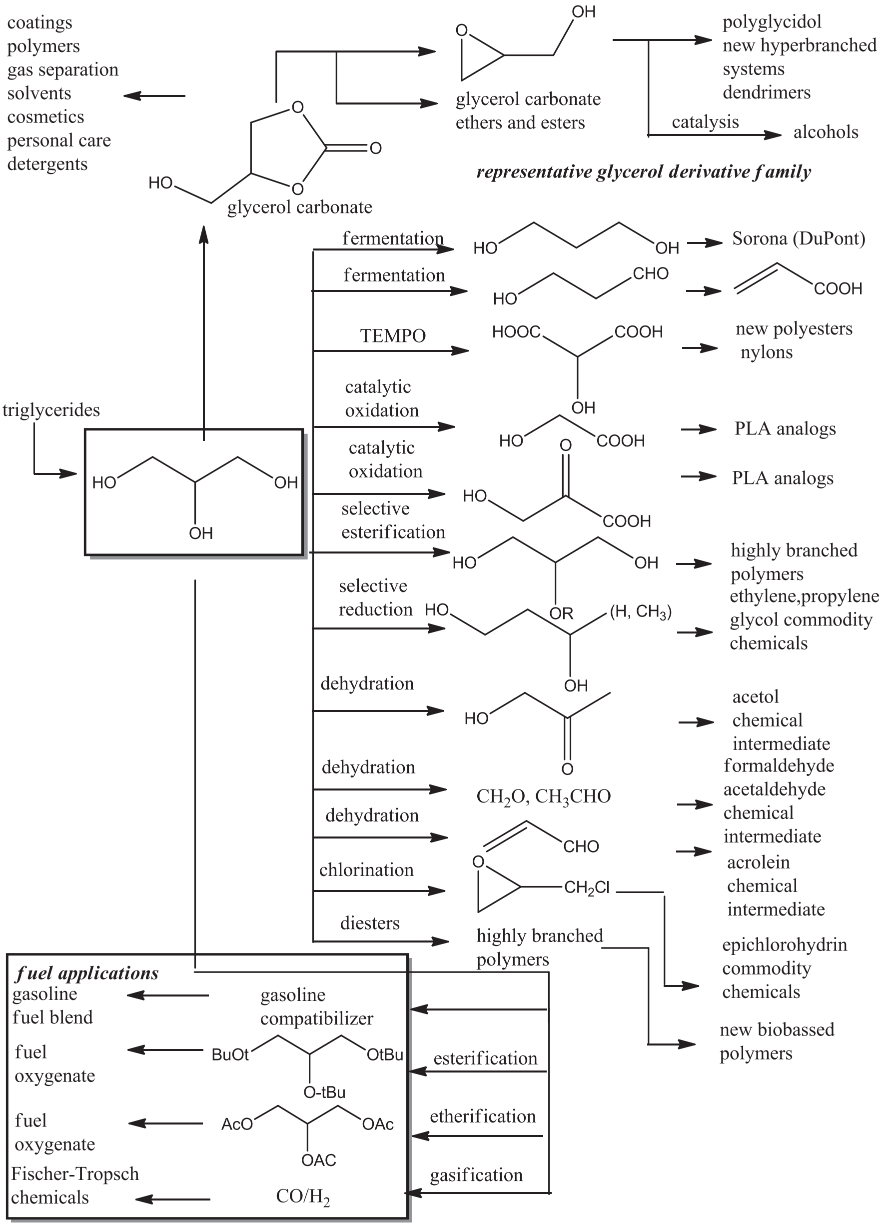
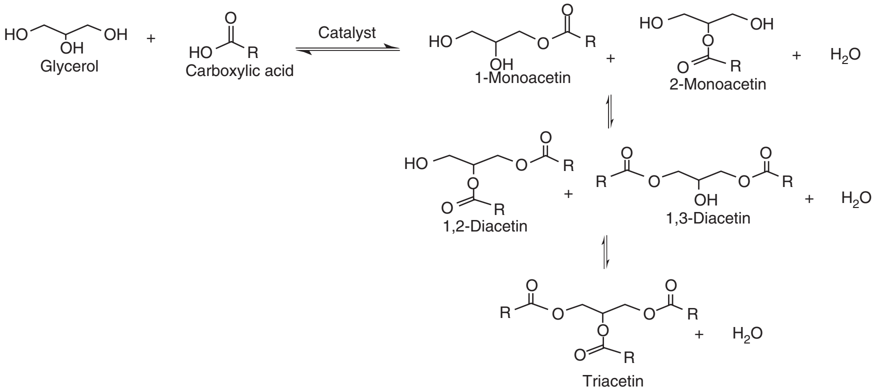


Fig. 30 Summary of the processes for conversion of glycerol into value-added chemicals, fuels and fuel additives (Reproduced from Bozell and Petersen [21])

improvements in catalysts for APR of glycerol is required. Conversion of glycerol to syngas by microwave plasma and supercritical water gasification of glycerol result in syngas production, which is to be converted further to yield hydrogen. These processes however require higher temperatures (500–650 °C) and low concentration of glycerol, 5–20% w/w [322].

Fuel additives, when blended with gasoline or diesel, help to improve viscosity and cold flow properties, anti-knock characteristics and octane rating and reduce emission of harmful exhaust gases (NOx) and particulates. They also ensure thermal stability and clean combustion of the fuel and prevent corrosion of engines. Some of the fuel additives that can be obtained from glycerol are *acetin (glycerol esters)*, *glycerol ethers*, *solketal and acetal*.

Esterification of glycerol with acetic acid or acetic anhydride using homogeneous and heterogeneous catalysts [326, 327] and transesterification of glycerides or glycerol with methyl acetate [328, 329] are known. Being a trihydric alcohol, acetylation of glycerol could lead to the formation of mono-, di- and triacetins, as illustrated in Scheme 10 [322]. While mono- and diacetins find applications in cosmetics, medicines and food industries and as monomers in the production of biodegradable polyesters, it is the triacetins which are useful as fuel additives. Esterification is basically an acid-catalysed reaction, and almost all types of heterogeneous acidic catalysts, starting from ion-exchange resins (Amberlyst-15), clays (K10-montmorillonite), zeolites (H-beta, HZSM-5, HSUY), niobic acid, heteropoly acids, sulfonic acid-functionalized mesoporous SBA-15, zirconia-based mixed metal oxides and sulphated zirconia-based catalysts, have been explored as catalysts. A list of such catalysts, reported recently, has been compiled by Nda-Umar et al. [322], and few examples are covered here. Though acetic acid is commonly employed as acetylating agent, use of acetic anhydride is advantageous due to better accessibility of acylium ion from the anhydride compared to the intermediate from acetic acid. Due to this reason, on H-beta and K10, with acetic anhydride, 100% selectivity for triacetin was achieved in 20 min at low temperature of 60 °C [330].



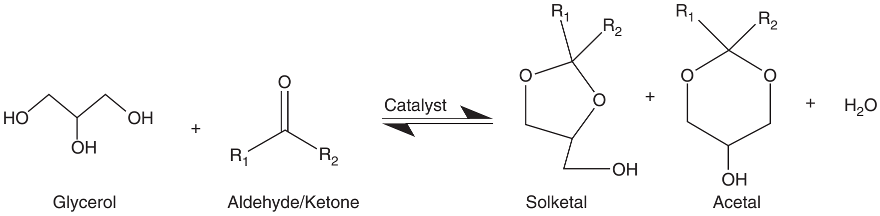
Scheme 10 Conversion of glycerol to acetins by esterification with carboxylic acid (Reproduced from Nda-Umar et al. [322])

On Amberlyst-15, with acetic acid as acylating agent, 90% glycerol conversion and 31%, 54% and 13% selectivity towards mono-, di- and triacetins could be realized. However, with acetic anhydride, on the same catalyst, 100% selectivity for triacetin was observed in 80 min at 60 °C. Iron oxide nanoparticles supported on mesoporous SBA-15 were highly active for glyceride formation with levulinic acid in the place of acetic acid, displaying >99% conversion of glycerol and 71% diacetin and 28% triacetin selectivity [331]. Sandesh et al. [332] have reported simultaneous synthesis of biodiesel and acetins using methyl acetate, on a series of novel solid basic catalysts, based on metal hydroxy stannates, MSn $(OH)_6$ with M = Mg, Zn, Sr and Ca. The catalyst with higher basicity, CaSn $(OH)_6$, exhibited glycerol conversion of 78.2%, with 67.3% monocetins and 32.6% diacetins selectivity. While complete conversion of glycerol could be realized, major research efforts are directed towards achieving desired acetin selectivity, by employing different catalysts and process conditions [322].

Glycerol ethers are useful as oxygenated fuel additives and solvents. Glycerol ethers are obtained by etherification of glycerol with olefins/alcohols (isobutene/tertiary butyl alcohol). Similar to acetins, glycerol mono-, di- and tri-ethers are formed. Different types of zeolites, clays, ion-exchange resins and supported heteropoly acids have been employed as catalysts [322]. Carbon supports derived from bio-resources like sugar cane bagasse, coconut husk and coffee grounds, after functionalization with sulphonic acid, proved to be highly effective for etherification of glycerol. 81.8% glycerol conversion with 60.5% selectivity to mono-ether and 21.8% to di- and tri-ethers could be obtained with carbon derived from sugar cane bagasse [333]. A comparative evaluation of ion-exchange resins (Amberlyst-15 and Amberlyst-35) and zeolites (Beta-BEA and USY and MOR) has shown that though the resin catalysts exhibit higher glycerol conversion at a lower temperature (75 °C) than zeolite-based catalysts (90–110 °C), the latter group of catalysts display higher stability, forming preferentially di- and tri-tertiary butyl glycerol. More than 95% glycerol conversion with 45% and 54% selectivity for di- and tri-tertiary butyl glycerol is realized on nanosize BEA catalyst, due to relatively larger-sized pores [334].

Glycerol formals are formed by reaction between glycerol and aldehyde or ketone as illustrated in Scheme 11.

Solketal is a highly useful fuel additive, known for reducing particulate emission and gum formation and improving cold flow characteristics and oxidation stability [335, 336]. More than 90% yield of solketal is obtained by condensation of glycerol



Scheme 11 Conversion of glycerol to solketal and acetal (Reproduced from Nda-Umar et al. [322])

and acetone using p-toluene sulfonic acid as the catalyst, with glycerol/acetone ratio of 1:6 [337]. Formation of ketals with several types of ketones besides acetone like butanone, cyclopentanone, 4-methyl-2-pentanone and 3,3-dimethyl-2-butanone was investigated by De Torres et al. [338]. In the condensation of glycerol and cyclopentanone, at a molar ratio 1:1 and at 60 °C temperature, 81.4% solketal was obtained with fluorosulfonic resins (NR-50 and SAC-13) and K10-montmorillonite as catalysts over a reaction time of 2 h. Condensation of glycerol with acetone in continuous-flow mode using several heterogeneous catalysts (Amberlyst wet, zeolite, Amberlyst dry, zirconium sulphate, montmorillonite and polymax) was investigated by Nanda et al. [339]. Under optimized process conditions of 25 °C, acetone/crude glycerol molar ratio of 4 and WHSV of 2 h^{-1}, maximum yield of 94 ± 2% solketal could be obtained [340] on Amberlyst wet catalyst, which could be regenerated and reused for another 24 h cycle, without any loss of activity.

Similarly, formation of *acetals* by condensation of glycerol with aldehydes, using different types of acidic catalysts, has been studied extensively [322]. Like ketals, acetals are useful as fuel additives and solvents in paint and pesticide industries. Umbarkar et al. [341] have studied acetalization of glycerol with different aldehydes on well-characterized mesoporous MoO_3/SiO_2. Maximum conversion of 72% benzaldehyde with 60% selectivity to acetal was observed on 20% w/w MoO_3/SiO_2 at 100 °C in 8 h. Recent developments in the catalysts and features in the processes for acetalization of glycerol have been covered in a review by Amin et al. [342].

Glycerol could be converted into a number of *value-added chemicals/chemical intermediates* (Fig. 30) through chemo- and bio-catalytic routes as described in several reviews [21, 91, 95–99, 322, 323]. Apparently simple conversion like dehydration of *glycerol to acrolein* has been the subject of intensive studies, mainly devoted to the development of catalysts that display maximum selectivity at optimum conversion and reasonable life/regenerability. Though Cs salt of heteropoly tungstic acid supported on silica displayed 100% glycerol conversion and 98% selectivity for acrolein, the stability of the active phase (leaching) was the challenge [343]. Similarly, on supported $NiSO_4$ catalyst, 90% glycerol conversion and 70% selectivity to acrolein could be achieved, but the catalyst was prone to deactivation due to oxidation and loss of sulphur [344]. Multicomponent catalyst with W-Zr-Al active phase, supported on hexagonal mesoporous silica (HMS) (MUICat-5), displayed excellent stability, higher glycerol conversion (86%) but moderate acrolein selectivity of 60% [345]. Though zeolite-based catalysts are active at high GHSV (1438 h^{-1}), selectivity for acrolein is low [346]. A compilation of catalysts for dehydration of glycerol from recent literature is presented in the review by Nda-Umar et al. [322]. Some of the strategies for extending the catalyst life and reactor design aspects are discussed in another monograph by Cognet and Aroua [323].

Glycerol carbonate (GC) is the other glycerol derivative with widespread applications in the manufacture of polyurethanes, polyesters, polycarbonates and polyamides and useful as substitute for fossil-derived ethylene carbonate or propylene carbonate. It is also used as solvent in the paint, battery and detergent industries as well as in the synthesis of very valuable intermediates such as glycidol. GC is prepared by three routes, by reacting glycerol with urea or dimethyl carbonate or by directly reacting it with carbon dioxide under supercritical conditions [322]. Transesterification of glycerol with ethylene carbonate over basic oxide catalysts (MgO, CaO) and mixed metal oxides of Al-Mg, Li-Al and Al-Ca-MO with hydrotalcite structure at 35 °C results in high conversion and >98% selectivity to GC [347]. Ionic liquid catalysts like 1-n-butyl-3-methylimidazolium-2-carboxylate could yield 93% GC in 5 h. With the ionic liquid 1-ethyl-3-methylimidazolium acetate as catalyst, glycerol conversion of 93.5%, selectivity of 94.9% and GC yield of 88.7% were obtained at optimum conditions of 120 °C, 0.5 mol.% catalyst loading, diethyl carbonate/glycerol molar ratio of 2 and reaction time of 2 h [348]. There was no deactivation even after the catalyst was used three times, which was attributed to excellent interaction between the ionic liquid and the reactant.

1,3-Propane diol is a versatile chemical intermediate and highly useful monomer for the production of polyesters (polytetramethylene terephthalate, PTT), polyethers, polyurethanes and many other value-added chemicals [322]. Hydrogenolysis of C-O bond in glycerol results in the formation of 1,2-propane diol (1,2-PDO) and 1,3-propane diol (1,3-PDO), with the selectivity for specific diol determined by the type of catalyst and the reaction conditions adopted. Hydrogenolysis, which involves dehydration as the first step, can result in the formation of hydroxy acetone, which on further hydrogenation leads to 1,2-PDO. If, on the other hand, the dehydration leads to the formation of 3-hydroxy propanal, its further hydrogenation results in 1.3-PDO [349]. Since formation of hydroxy acetone is favoured thermodynamically, 1,2-PDO is formed with high selectivity on many types of catalysts, noble metal, non-noble metal or noble metals in combination with acidic/basic components [98–102]. However, 1,3-PDO with high selectivity of 66% is observed only with noble metal- mixed oxide catalysts, like Pt-WO_x/AlOOH with moderated acidity [100]. Though a large number of other catalyst systems, mono- and bimetallic catalysts with different supports, have been explored [322, 349], maximum 1,3-PDO selectivity of 52% could be realized. On Ir-ReO_x/SiO_2 catalyst, Nakagawa et al. [349] could observe 1,3-PDO selectivity of 65% but at lower glycerol conversion of 22.6%. Thus, achieving high conversion of glycerol with high selectivity for 1,3-PDO on heterogeneous catalysts remains a challenge. Biochemical conversion of glycerol to 1,3-PDO, using different microorganisms like *Bacillus*, *Lactobacillus*, *Klebsiella*, *Citrobacter*, *Ilyobacter*, *Enterobacter and Clostridium*, in batch and continuous mode processes, has been reported [350].

Glycerol as biochemical feedstock has gained prominence when it replaced glucose as the raw material for the enzymatic conversion to 1,3-PDO [21]. With glycerol as the feedstock, 1,3-PDO yields approaching to the theoretical yield (g of 1,3-PDO per g of feed) of 67% could be achieved with genetically modified *Clostridium acetobutylicum* with concentrations of over 84 g L^{-1} at a rate of 1.7 g L^{-1} h^{-1}. In contrast, with glucose as feedstock, the yield was 30–40% only [351, 352]. Fermentation of *crude glycerol* with *Clostridium acetobutylicum* [353] and *Klebsiella pneumoniae* [354] resulted in the same level of PDO concentration and productivity realized with purified glycerol, thus paving way for the utilization of crude glycol as economically viable bio-resource for the production of 1,3-PDO.

Utilization of crude glycerol as biochemical feedstock for 1,3-PDO has brought into focus the production of several other important chemicals/chemical intermediates through enzymatic processes. Microbial processes with crude glycerol as feedstock have been reported for the production of hydrogen, methanol, ethanol, n-butanol, glyceric acid, citric acid, polyunsaturated fatty acids, lactic acid, succinic acid and biopolymers like poly hydroxy alkanoate (PHA), poly hydroxy butyrate (PHB) and acrylates. Development of microbial processes for these chemicals, types of microorganisms employed and the process conditions adopted have been covered in detail in the reviews by Dobson et al. [355] and Garlapati et al. [356].

Oligomerization of glycerol to polyglycerol and conversion to olefins (ethylene, propylene and butadiene) are the other processes that utilize glycerol as raw material [322].

Though a number of processes have been developed and patented [322] for the conversion of glycerol to value-added chemicals, fuels and fuel additives, only few of them have reached commercial scale. Epichlorohydrin from glycerol (Dow, Solvay) via dichloro propanol [21], 1,3-PDO using recombinant *Escherichia coli* (DuPont) and polyglycerols by Sakamato Japan have been successful on commercial scale. Tremendous opportunities as well as challenges remain in glycerol conversion processes, requiring continuous research efforts to improve process efficiency, selectivity, catalyst stability and reduction in the cost of production, to enable viability on commercial scale.

8 Conversion of Furfuryl Alcohol into Fuels and Chemicals

Furfuryl alcohol (FOL) is one amongst the most important derivatives of furfural (FAL), another abundant biomass intermediate and a versatile platform chemical [357]. More than 65% of FAL is utilized for the manufacture of FOL by catalytic hydrogenation, which has been studied extensively [357, 358]. Major applications of FOL derivatives towards production of value-added chemicals/fuels are illustrated in Fig. 31.

An important derivative of FOL is *levulinic acid* (LA, 4-oxopentanoic acid), which is one amongst the 12 platform chemicals identified by US DOE in 2004, with tremendous application potential. Global market for LA during the period 2019–2024 is projected to grow at CAGR of 4.9%, to touch US$ 34.5 Mill. by 2024 [359]. As many as 16 different application segments for LA have been listed by Bozell et al. [360]. LA can be produced from lignocellulosic biomass via the Biofine process [361] and also from FOL by acid-catalysed ring opening in H_2O [362]. LA with two active functional groups (keto and carboxyl) undergoes a range of chemical transformations (Fig. 32) yielding highly useful chemicals and fuels. Salient features of these transformations brought out by different catalysts have been covered in the reviews by Bozell et al. [360], Mariscal et al. [357] and Xue et al. [363].

Delta-aminolevulinic acid (DALA), another derivative of LA, is useful as biodegradable broad-spectrum herbicide/insecticide and for cancer treatment [360].

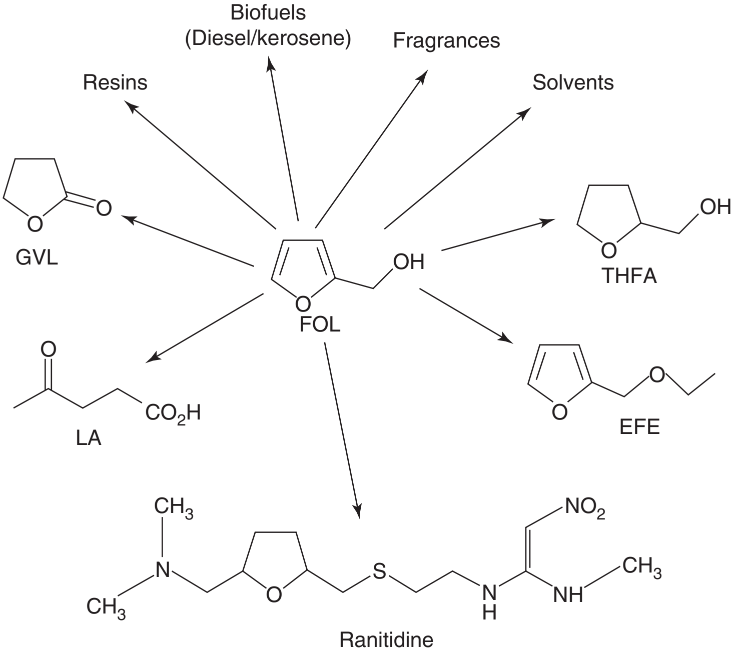
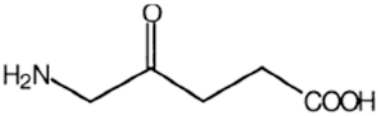


Fig. 31 Value-added products from furfuryl alcohol (Reproduced from Mariscal et al. [357])



Delta-aminolevulinic acid (DALA).

Other derivatives like methyltetrahydrofuran, γ-valerolactone (GVL) and esters of levulinic, valeric and pentanoic acids find applications as fuels and fuel additives [357].

Alkyl levulinates (AL) or esters of levulinic acid, especially with ethanol and butanol, belong to a class of highly efficient bio-based fuel additives for blending with gasoline and diesel, due to low sulphur content and toxicity, high lubricity, good flow properties and flash point stability [357, 364]. Several routes based on solid acid catalysts for synthesis of AL from different raw materials like (1) levulinic acid, (2) mono- and disaccharides (glucose, fructose, sucrose), (3) polysaccharides and biomass and (4) furfuryl alcohol have been investigated in detail and been covered extensively in the reviews by Ahmad et al. [364] and Demolis et al. [365]. Ionic liquids [IL]-based and sulfonic acid-functionalized catalysts are reported to be promising candidates for these processes [364]. Though direct synthesis of AL from cellulosic biomass is possible, due to its complex structure, the process involves several steps like depolymerization, solvolysis, dehydration and alcoholysis and requires relatively severe process conditions and hence lower selectivity/yields in comparison with those from LA or FOL.

Etherification of FOL with ethanol yields (Scheme 12) *ethyl furfuryl ether* (EFE), an efficient fuel additive. Synthesis of EFE using ZSM-5 and zeolite beta catalysts and its blending characteristics with gasoline up to 30% w/w have been reported by Haan and Lange [366, 367].

Especially with ZSM-5 (SAR-30) catalyst, and ethanol/FOL molar ratio of 7.5:1, EFE yield of 50% could be achieved with 80% conversion of FOL at 398 K by Lange et al. [368]. Though some amount of (<10 mol.%) useful side products like LA and angelica lactone could be observed, formation of ~20 mol.% of heavier products points out the need for further improvements in the process, in terms of

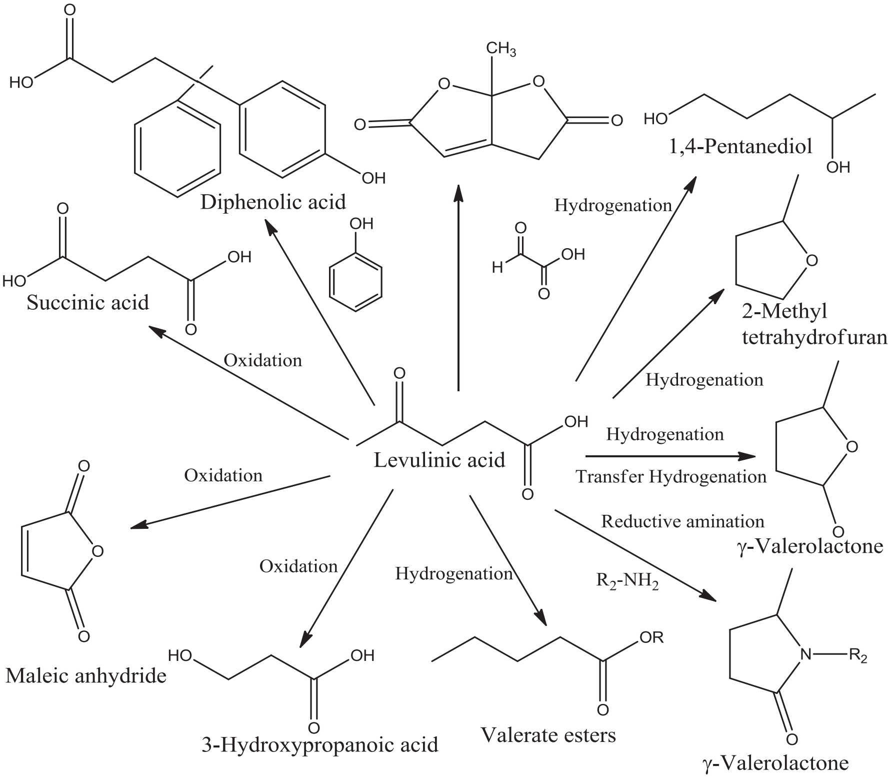
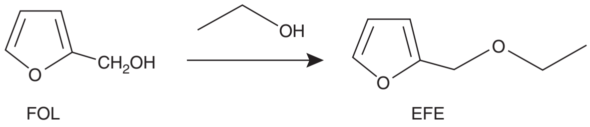
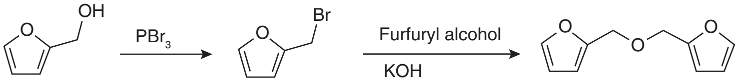


Fig. 32 Chemical transformations of levulinic acid to value-added chemicals and fuels (Reproduced from Xue et al. [363])

Scheme 12 Etherification of furfuryl alcohol to ethyl furfuryl ether





Scheme 13 Synthesis of DFE from FOL

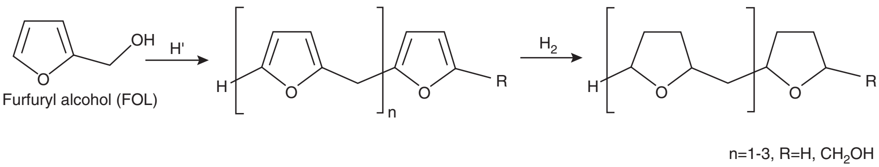
alternative more selective catalysts and optimization of process conditions and arresting the deactivation of catalysts. *2,2′-Difurfuryl ether* (DFE), a well-known flavouring agent in the food industry, is obtained from FOL, by conventional two-step process [369] involving bromination of FOL followed by etherification (Scheme 13).

DFE is also formed as by-product during oligomerization of FOL [370] and by direct etherification using polyoxometallate catalysts [369].

By carrying out appropriate modifications in the catalyst formulations and optimization of process conditions (to achieve ring/side-chain or total hydrogenation), three more useful derivatives of FOL, namely, tetrahydro furfuryl alcohol (THFOL), methyl furan (MF) and methyltetrahydrofuran (MTF), with specific individual applications as chemicals and fuels [357, 358, 368], could be obtained.

Highly controlled o*ligomerization and polymerization* of FOL yield a range of useful materials/composites [371–373]. Oligomerization of FOL (in homogeneous phase with H_2SO_4 or Amberslyst-15 ion-exchange catalyst in heterogeneous phase) followed by hydrogenation on Ni/Al_2O_3 catalyst (Scheme 14) results in C_9–C_{20} hydrocarbons useful as diesel/kerosene range blends [357, 374] and fuels.

Besides being the raw material for the manufacture of numerous chemicals and fuels, the most important application of FOL, in terms of consumption volume (~88%), is for the manufacture of resins. Exothermic condensation polymerization of FOL in the presence of aqueous acid solution proceeds in two modes, the first one being alkylation at C_5 position of the furan heterocycle (forming a methylene bridge, with head-to-tail structure) and the second involving the condensation of two −OH groups (etherification, with head-to-head structure) as depicted in Fig. 33. However, on elimination of formaldehyde from ether linkages, head-to-head configuration transforms into head-to-tail structure. The resinification process, besides being highly exothermic, is also autocatalytic, requiring efficient heat removal and careful control of pH, to avoid any possible explosion [375]. Inorganic (H_2SO_4 HCl and HNO_3) and organic (p-toluene sulfonic, dodecyl benzene sulfonic, formic, lactic, maleic and oxalic) acids and Lewis acids $SnCl_4$ and $TiCl_4$ have been employed as catalysts for resinification of FOL. This is followed by curing process, wherein conjugated polyfurfuryl chains undergo interchain Diels-Alder condensation leading to cross-linking [357]. When solid acid catalysts are used, they get incorporated in the resin matrix, forming polymer-based nanocomposites (PNC) with improved properties [376]. Such cross-linked polymers of FOL possess excellent chemical, thermal, corrosion resistance and mechanical properties, thus rendering them highly useful for applications in foundry industry and for coatings, wood protection, fibre-reinforced plastics, adhesives and binders, low-flammability materials, membranes and fabrication of electronic materials. Hazards due to emission of formaldehyde, generally associated with formaldehyde-based resins, are avoided with the use of FOL-based resins.



Scheme 14 Oligomerization-hydrogenation of FOL to diesel/kerosene blends [357]

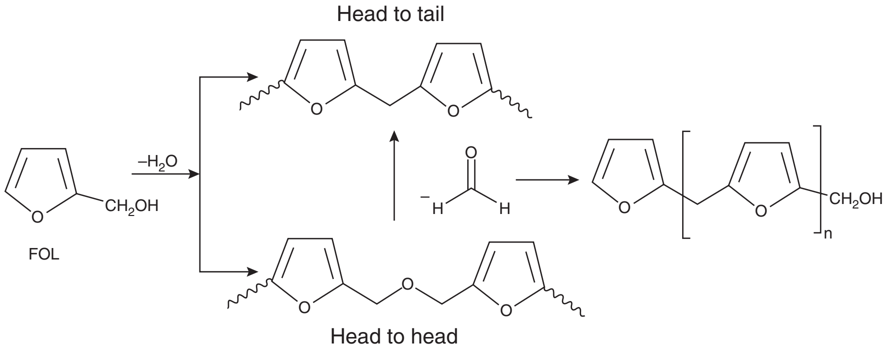
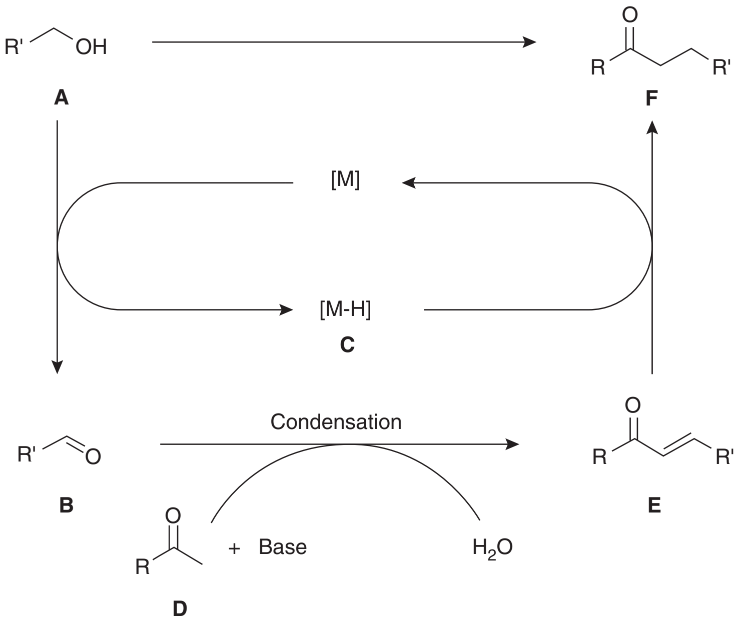


Fig. 33 Acid-catalysed condensation polymerization of FOL [357]

9 Miscellaneous Conversions of Alcohols

Oxygenates of alcohols, namely, aldehydes, ketones, acids, ethers and esters, are important class of derivatives, useful mainly as solvents, raw materials and intermediates for the synthesis of value-added products. Depending on the type of catalysts (usually supported metal/metal oxide) and the process conditions, different oxygenated products are formed. Dehydration, dehydrogenation, oxidative dehydrogenation, etherification, oxidation and esterification are the typical reactions involved. Synthesis and applications of oxygenates from ethanol have been studied extensively and reviewed [166, 377, 378]. Simplest of all is the conversion of ethanol to diethyl ether (DEE) by vapour phase acid-catalysed dehydration of ethanol. On gamma alumina [379], DEE with 80% selectivity is obtained, while on heteropoly acid catalyst [380], nearly 100% selectivity could be achieved. While monofunctional supported copper catalysts are active for acetaldehyde formation via dehydrogenation, supported gold catalysts, on the other hand, catalyse oxidative dehydrogenation of ethanol to yield acetaldehyde [377]. A bi-functional redox-acidic catalyst [Cu/ZrO_2] further transforms acetaldehyde into ethyl acetate by reaction with ethanol. It is proposed that a pair of Cu^0/Cu^{+1}sites present at metal/support interface facilitate further reaction of acetaldehyde and ethanol to ethyl acetate [381]. Both liquid phase (supported Au catalysts) and vapour phase (supported Mo-V-Nb catalysts) oxidation of ethanol to acetic acid have been reported. Cu-doped Au/NiO is found to be highly active at 120 °C in aqueous phase oxidation of ethanol to acetic acid with >90% selectivity [377]. However, the process is not viable on industrial scale, wherein carbonylation of methanol with CO in homogeneous phase, with Rh/Ir complexes (Monsanto/CATIVA processes), is the preferred route.

Alkylation with alcohols is a well-known reaction, and catalytic alkylation of aromatics with alcohols is a well-established process in petrochemical industry. Recently *alpha-alkylation* reactions of various substrates with alcohols via hydrogen borrowing cycle are being pursued extensively [382]. Scheme 15 presented below describes the mechanistic pathway involved in the process, which starts with the transfer of hydrogen from alcohol A to the metal M, resulting in the formation of aldehyde B and metal hydride C. Base-catalysed aldol condensation of aldehyde B with the substrate carbonyl compound D leads to the formation of αβ-unsaturated ketone E, which undergoes hydrogenation through metal hydride to yield the alpha-alkylated product F. The process, resulting in the formation of C-C bonds via C-alkylation in presence of various transition metal catalysts and a base, has widespread applications in synthetic organic chemistry and been studied extensively. Different types of carbonyl substrates, like aldehydes, ketones, esters, amides [383], nitriles, acetonitrile, acetamides, methyl pyrimidines and methyl quinolines [382], with appropriate catalysts, undergo alpha-alkylation with alcohols. Besides the traditional transition metal-based catalysts, homogeneous catalysts, for instance, Mn-based pincer complexes [383] and Os- and Ir-based complexes, and heterogeneous catalysts, especially supported transition metal catalysts and Pd and Ni



Scheme 15 Alpha-alkylation of typical carbonyl compound with alcohol (Reproduced from Ref. [382], Obora Y)

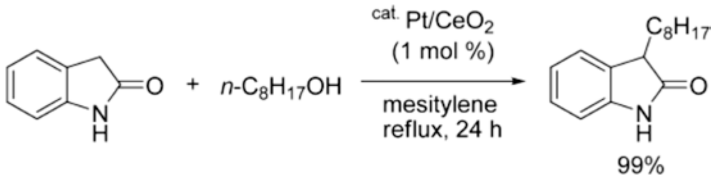
nanoparticles immobilized on inorganic supports, have been explored for alpha-alkylation [382]. Typical examples of such conversions are presented for illustration.

Shimizu et al. [384] have reported selective C-3 alkylation of oxindole (1 mmol) with 1-octanol (1.1 mmol) using 1% Pt supported on CeO_2 catalyst in mesitylene as solvent (1.5 g) at 170 °C for 24 h (Scheme 16) which could achieve 99% yield of alkylated product.

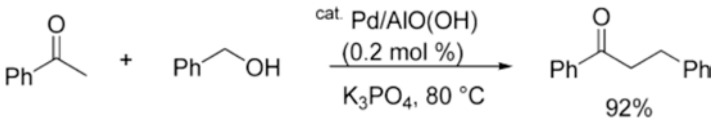
Alkylation of acetophenone (1 mmol) with benzyl alcohol (1.2 mmol) on nano-scale Pd particles supported on AlO(OH) catalyst in presence of K_3PO_4 (3 mmol) at 80 °C in Ar atmosphere results in 92% yield of alkylated product in 8 h (Scheme 17).

N-alkylation of amines and nitroarenes is another important step in synthetic organic chemistry. Dimethyl carbonate (DMC), dimethyl sulphate (DMS), methyl iodide (MI) and methanol are commonly used as methylation reagents. Comparative evaluation of these reagents on green chemistry metrics (atom economy, mass index) has shown that both DMC and methanol provide safer and greener reactions [387]. Hence methanol/alcohols are preferred reagents for N-alkylation of amines and O-methylation of phenols. Another desirable criterion is the selective N-monomethylation vs. overalkylation. Recently, Fu et al. [388] have developed an active and reusable Ir@YSMCNs nano catalyst (iridium nanoparticles encapsulated within yolk-shell-structured mesoporous carbon nanospheres) which is highly effective for selective mono N-methylation of amines and nitroarenes. The reaction follows again the hydrogen borrowing cycle, with methanol acting as hydrogen donor, as depicted in Scheme 18. On Ir@YSMCNs catalyst (0.5 g, 4% Ir loading), in presence of t-BuOK (1 mol. eq.) as base and 2 mmol of aniline in methanol (15 ml) at 170 °C, 92% conversion of aniline with 97% selectivity for N-mono methyl aniline could be achieved.

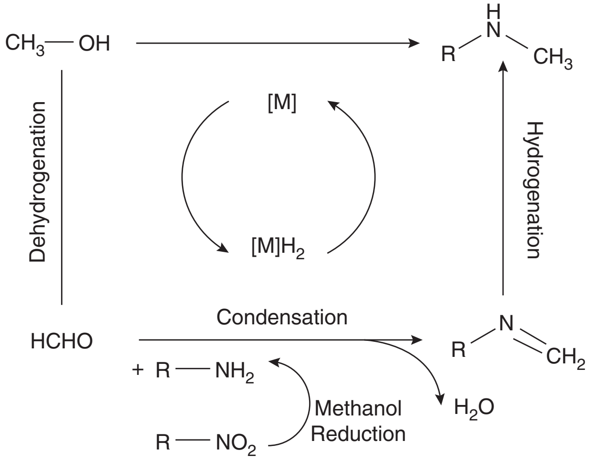
Under optimized reaction conditions (2 mmol of nitrobenzene in 15 ml methanol, 2 mmol of t-BuOK, 0.15 g catalyst with 4% Ir loading and at 170 °C), complete conversion of nitrobenzene with 97% selectivity towards N-monomethylated aniline could be realized in 30 h. Nitro compounds with different substituents could undergo facile conversion with high yields of N-monomethylated anilines on Ir@



Scheme 16 Selective alpha-alkylation of oxindole (Reproduced from Shimizu et al. [384])



Scheme 17 Alpha-alkylation of acetophenone (Reproduced from Kwon et al. [385, 386])



Scheme 18 Mechanism proposed for N-monomethylation of nitroarenes and amines with methanol via borrowed hydrogen cycle pathway (Reproduced from Fu et al. [388])

YSMCNs catalyst under optimized reaction conditions. In both cases [385, 386, 388], though hydrogen borrowing is envisaged, the actual step could be hydride/hydrogen transfer.

Jiang et al. [389] have reported the application of reusable, commercial 5% Pd/carbon catalysts for selective N-mono methylation of various aniline substrates with high yields, in presence of a base CH_3ONa under mild reaction conditions. Besides methanol, other alcohols also could be used as alkylation reagents, thus rendering alcohols as highly efficient alkylation reagents.

10 Future Trends

Currently, the global energy scenario is in the midst of a paradigm shift, with the emphasis on the generation of clean energy through environmentally sustainable processes. The chemical industry, on its part, is on the lookout for low-carbon energy, renewable feedstocks and more efficient as well as sustainable process technologies. The existing fossil resources as the raw material inventory for the refineries/chemical industries are gradually getting replaced with renewable bio-sources, carbon oxides from industrial waste gases and solid wastes [32–35, 53–56, 390]. Accordingly, the chemical process slate is also changing its face. In this context, production of bio-methanol/ethanol and other alcohols from renewable resources through chemo/bio-catalytic processes and their subsequent conversion to fuels and other value-added products have reached commercial status already, though limited in number, as of now.

Besides the technological challenges associated with conversion of bio-based feedstocks, the cost of production through sustainable routes has been a major limiting factor in this endeavour. The cost of production of ammonia, methanol, olefins (ethylene, propylene) and aromatics (benzene, toluene, xylenes), which together account for nearly two thirds of GHG emissions from the chemical industry, would be significantly higher, if alternative renewable feedstocks were to be used as of now [391]. Comparison of cost of production of fuels and chemicals from fossil vs. renewable resources has been a subject of in-depth study from time to time, since the early 1980s [392, 393]. However, it remains only indicative, due to the wild variations/shocks (Fig. 34) in the price of crude oil, which is governed by several extraneous factors other than availability, exploration and production issues, like climate conditions/control, various types of geo-political environments/compulsions/tensions, frequent demand-supply imbalances and, of recent, a global pandemic. In the year 2007, Rass-Hansen et al. [393] have indicated the relative cost of some selected chemicals (Fig. 35) derived from fossil and renewable resources, based on the cost of the raw materials prevalent at that time. It is observed that the cost of production of ethanol, ethylene and acetic acid from renewable resources is lower vis-à-vis the cost from fossils, possibly due to high crude oil price in 2007. The scenario is bound to change with the volatility in crude oil price.

As we move on into the future, the societal benefits due to clean environment, low-carbon energy and sustainable chemical processes may outweigh the indicative cost differentials, with technological innovations taking the centre space. Hence, the major future research focus in the area of alcohol conversion processes would be towards improving overall process efficiency. Some of the key areas that need further investigations/improvements/innovations are:

- Further reduction in the cost of production of bioethanol from lignocellulosic biomass is needed to remain competitive vis-à-vis raw materials/fuels from fossil sources [163, 164, 394–396]. Especially the pretreatment and fractionation of biomass into major components/active intermediates/platform molecules continue to be challenging and add to the cost. Strategies to co-produce value-added products along with ethanol from biomass [53] are to be pursued vigorously to reduce the cost.

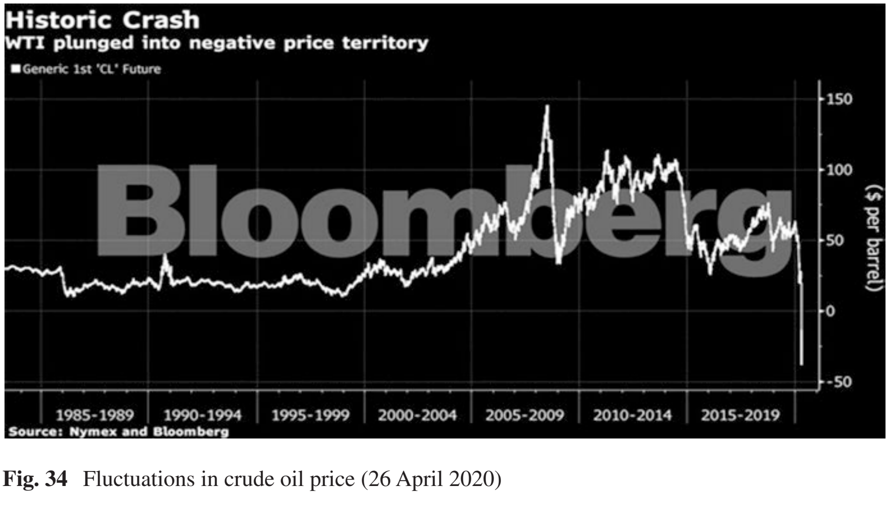


Fig. 34 Fluctuations in crude oil price (26 April 2020)

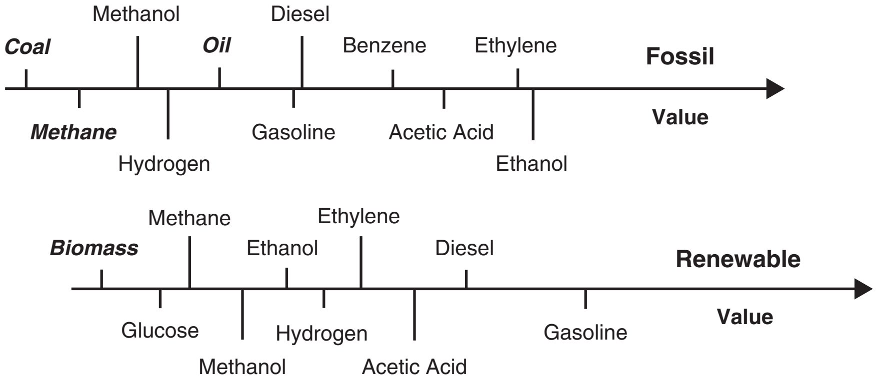


Fig. 35 Relative cost of selected chemicals derived from either fossil or renewable sources [393]

- A closely related area of concern is the separation and purification of products. In many biomass conversions by chemo- as well as bio-catalytic routes, a number of side products are formed, and developing innovative and more efficient separation and purification technique for maximum recovery of desired product(s) could boost the process efficiency.
- Though production of acetone, butanol and ethanol (ABE) process has been in practice for a number of years now, the high cost of hydrolytic enzymes and the need for expensive pretreatment steps are still the challenges that have to be addressed. The success and adaptability of ABE and other enzymatic processes for 1-butanol and other alcohols depend on the choice of microorganism species, their genetic manipulation and process optimization along with substrate. Recent developments in these aspects have led to renewed interest in bio-catalytic processes for the production of alcohols [397–399].
- Developing active, selective and stable catalysts for alcohol/biomass conversion processes has been a challenge, especially to maximize selectivity and retard deactivation. Amongst the different possible reaction pathways, the desirable one needs to be catalysed, by incorporation of requisite catalytic functionalities. Highly reactive molecule like glycerol can undergo several transformations, as illustrated in Fig. 30. To maximize the yield of a specific product, both metal and acidic/basic sites need to be fine-tuned, which requires a thorough understanding of the reaction pathways and generation of appropriate active sites. In-depth characterization of used/deactivated/spent catalysts could provide vital clues to understand the process of deactivation and devise means of arresting the same. Such an approach needs more in-depth studies on the reaction kinetics and mechanism, supported by advanced in situ spectroscopic investigations and computational approaches.
- A number of alcohol conversion processes like ethanol to propylene/isobutene/aromatics; various conversions of glycerol, sugar alcohols and furanics; and aqueous phase reforming process require more systematic studies to develop

catalysts with higher selectivity and stability and improvements in overall process efficiency.

- Though the process for the conversion of ethanol to 1,3-butadiene (BD) has successfully met all the criteria for sustainability, the process economics is not favourable since BD production rate (grams of BD produced per hour per unit weight of the catalyst) is to be improved, which requires the development of superior catalysts [200, 205, 207, 229]. In this respect, 90% conversion of ethanol with 70% selectivity and high productivity rate of 0.4 g BD/g of catalyst/hr. on Ag/ZrO_2-SiO_2 reported by Dagle et al. [400] is noteworthy.
- Development of single-pot conversion processes, especially for versatile chemicals like levulinic acid/alkyl levulinates [364, 365], GVL and other furan derivatives, fuels and fuel additives [357], which utilize biomass intermediates and neat platform chemicals as raw materials, is the right approach. Synthesis of these chemicals directly from lignocellulosic biomass, though challenging, would be desirable. Designing multi-functional catalysts with appropriate active sites and a re-look on separation and purification steps are the key issues.
- Processes based on aldol condensation of alcohols with aldehydes and ketones and self- and cross-aldol condensation of alcohols (Guerbet alcohols) are highly important steps in C-C bond formation [27, 241] and synthesis of highly useful fuels and chemicals and, in general, in many biomass conversion processes. Dual functional catalysts involving metal (for dehydrogenation and hydrogenation) and acid-base sites (for aldol condensation) are required. There are still questions regarding the role of the key intermediates in these reactions, and the exact nature of the acid-base sites responsible for generation of critical intermediates is yet to be established. Various supports like hydroxyapatite, hydrotalcites, γ-Al_2O_3 and MgO with several modifiers and reducible of the metal ions (Ni. Cu, Ru, Pd) have been explored for the conversion of ethanol to butanol [73–78]. However, the mode of functioning of the catalysts is not clear, though the general consensus is that low ratio of acid-base sites of the support may favour this reaction. Similarly, the criterion to be used for identifying the ease of reducibility of metal ions is yet to specified [401].
- Several promising processes have been developed for the conversion of alcohols to jet fuels and middle distillates/diesel [241, 282]. As the demand for these types of fuels is set to increase, the future research focus in this area would be towards a better understanding of oligomerization and aldolization chemistries that constitute the backbone for these routes. Studies in these and related areas would be helpful in improving the process efficiency.

11 Summary and Conclusions

Tremendous potential of biomass as feedstock for fuels and chemicals was visualized as early as 1981 by Lipinsky [392], when the biomass conversion processes were at primitive stage.

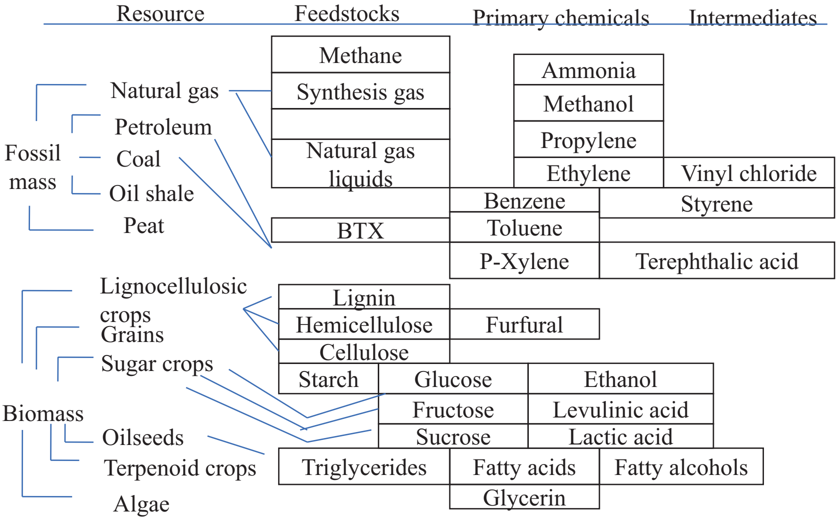


Fig. 36 Relationship between resources, feedstocks, primary chemicals and intermediates (Reproduced from Lipinsky [392])

The relationship (Fig. 36) between the two major resources, fossil and biomass, and their transformation into feedstocks, primary chemicals and intermediates, as envisaged at that stage, included biomass-derived *ethanol*, *glycerol*, *levulinic acid*, *lactic acid and furfural*, which were identified later, as versatile platform molecules, in 2010 [20, 21]. Since then, the development of processes for economically viable production of different types of alcohols through sustainable routes and a wide range of alcohol conversion processes have received global attention. Besides the traditional biomass resources, carbon oxides from industrial waste gases, solid wastes and other renewables [32–35, 257] have been explored as feedstocks for alcohols, thus enormously improving their availability at lower cost through low-carbon sustainable routes.

Alcohols with highly reactive R-O and O-H linkages are amenable for several types of catalytic transformations, yielding a range of fuels and chemicals. A compilation of major alcohol conversion processes developed over a period of time and the typical product slates in each case is presented in Fig. 37. A brief account of the origin of these processes, catalysts used therein, recent developments and future directions for research has been covered in this chapter.

Nearly, all types of fuels derived from fossil resources could now be produced from alcohols, besides highly efficient and new range of bio-based fuel additives, like alkyl levulinates and furfural/furan/furfuryl alcohol derivatives. Amongst the building block chemicals, production of ethylene and propylene in *on-purpose* mode, through MTO and MTP processes, has been well-established on commercial scale. Three *renewable methanol* production processes, developed by Carbon Recycling Institute (CRI), BioMCN and Enerkem, have successfully completed

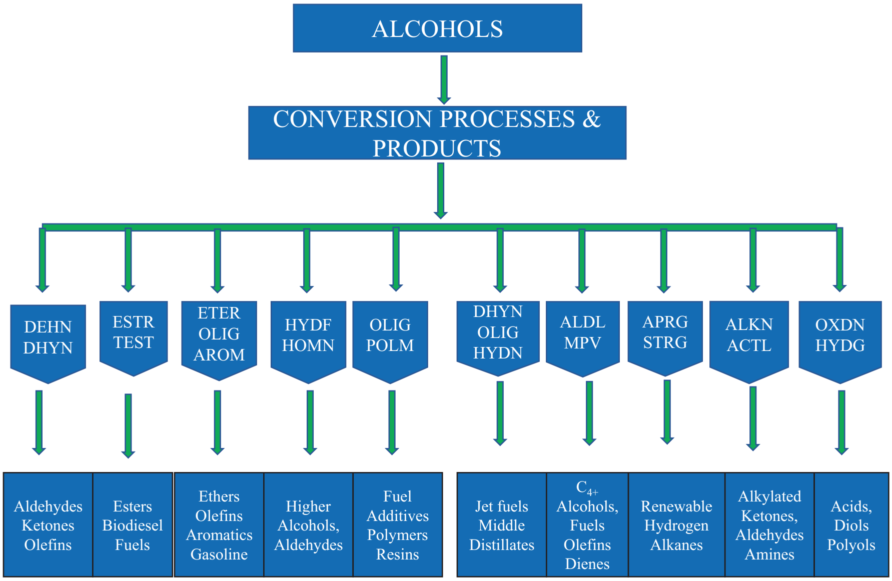


Fig. 37 Conversion processes and products from alcohols. *DEHN/DHYN* dehydrogenation/dehydration, *ESTR/TEST* esterification/trans-esterification, *ETER/OLIG/AROM* etherification/oligomerization/aromatization, *COPL/HOMN* coupling/homologation with CO, *OLIG/POLM* oligomerization/polymerization, *DHYN-OLIG-HYDN* dehydration-oligomerization-hydrogenation, *ALDL/MPV* aldolization Meewrwein Pondorrf Varley reaction, *APRG/STRG* aqueous phase reforming/steam reforming, *ALKN/NALK* alkylation/N-alkylation, *OXDN/HYDG* oxidation/hydrogenolysis

pilot/demonstration stage runs, and commercial-scale plants are under planning [32–35]. Once *renewable methanol* is available on commercial scale, MTO and MTP processes could, in the near future, become viable low-carbon alternatives to the olefins production by conventional steam cracking process. Similar developments could be envisaged for MTG and ETG processes as well, with the emphasis on improving the stability of the catalysts. 1,3-Butadiene from ethanol is another process with high promise, wherein the productivity rate is to be improved.

ASTM approval for the blending of bio-jet fuels produced by catalytic conversion of alcohols/other renewables (Lanza-PNNL and other processes) is a significant milestone in the area of biofuels. This development is expected to help the aviation industry in realizing the objective of reducing emissions by 50% (with respect to 2005 emission levels) by 2050, by substituting fossil-derived jet fuels with low-carbon bio-based fuels.

Alcohols have proven to be one of the most important sources for fuels and chemicals. Recent developments, as exemplified in this chapter, underpin the pivotal role that the catalytic transformations of alcohols could play, in building low-carbon sustainable society. Developments in large-scale production of renewable hydrogen from water, via photovoltaic-powered electrolysis, could greatly contribute towards improving the sustainability of processes based on alcohols. Such a scenario is bound to motivate sustained and more focused research efforts in this area, especially towards addressing the issues enlisted earlier and simultaneously seeking new avenues for growth.

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References

1. Huber GW, Iborra S, Corma A (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem Rev 106:4044–4098. https://doi.org/10.1021/cr068360d
2. Corma A, Iborra S, Velty A (2007) Chemical routes for the transformation of biomass into chemicals. Chem Rev 107:2411–2502. https://doi.org/10.1021/cr050989d
3. Alonso DM, Bond JQ, Dumesic JA (2010) Catalytic conversion of bi omass to biofuels. Green Chem 12:1493–1513. https://doi.org/10.1039/C004654J
4. Huber GW, Chheda JN, Barrett CJ, Dumesic JA (2005) Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. Science 308:1446–1450. https://doi.org/10.1126/science.1111166
5. Climent MJ, Corma A, Iborra S (2011) Converting carbohydrates to bulk chemicals and fine chemicals over heterogeneous catalysts. Green Chem 13:520–540. https://doi.org/10.1039/C0GC00639D
6. Demirbaş A (2001) Biomass resource facilities and biomass conversion processing for fuels and chemicals. Energy Convers Manag 42(11):1357–1378. https://doi.org/10.1016/S0196-8904(00)00137-0
7. Fang Z, Smith RL Jr, Qi X (2019) Resources in biomass and biorefineries, vol 9. Springer, New York, NY
8. Zhou C-H, Xia X, Lin CX, Tonga DS, Beltramini J (2011) Catalytic conversion of lignocellulosic biomass to fine chemical and fuels. Chem Soc Rev 40:5588–5617. https://doi.org/10.1039/C1CS15124J
9. Hayes DJ (2009) An examination of biorefining processes, catalysts and challenges. Catal Today 145:138–151. https://doi.org/10.1016/j.cattod.2008.04.017
10. Fernando S, Adhikari S, Chandrapal C, Murali N (2006) Biorefineries: current status, challenges and future direction. Energy Fuel 20:1727–1737. https://doi.org/10.1021/ef060097w
11. Pileidis FD, Titirici MM (2016) Levulinic acid biorefineries: new challenges for efficient utilization of biomass. ChemSusChem 9:562–582. https://doi.org/10.1002/cssc.201501405
12. Serrano-Ruiz JC, Dumesic JA (2011) Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. Energy Env Sci 4:83–99. https://doi.org/10.1039/C0EE00436G
13. Kamm B, Kamm M (2004) Principles of biorefineries. Appl Microbiol Biotechnol 64:137–145. https://link.springer.com/article/10.1007/s00253-003-1537-7
14. Kamm B, Gruber PR, Kamm M (2006) Biorefineries-industrial processes and products. Weinheim, Wiley-VCH Verlag GmbH &Co. K GaA
15. Kamm B (2007) Production of platform chemicals and synthesis gas from biomass. Angew Chem Int Ed 46:5056–5058. https://doi.org/10.1002/anie.200604514
16. De Jong E, Jungmeier G (2015) Biorefinery concepts in comparison to petrochemical refineries. In: Pandey A, Hofer R, Taherzadeh M, Nampoothiri M, Larroche C (eds) Industrial biorefineries and white biotechnology, 1st edn. Elsevier, Amsterdam, pp 3–33

17. Bozell JJ (2010) Connecting biomass and petroleum processing with a chemical bridge. Science 329:522–523. https://doi.org/10.1126/science.1191662
18. Somerville C, Youngs H, Taylor C, Davis SC, Long SP (2010) Feedstock for lignocellulosic biofuels. Science 329:790–791. https://doi.org/10.1126/science.1189268
19. Kohli K, Prajapati R, Sharma BK (2019) Bio-based chemicals from renewable biomass for integrated biorefineries. Energies 12:233. https://doi.org/10.3390/en12020233
20. Werpy T, Petersen G, Aden A, Bozell J, Holladay J, White J, Manheim A et al (2004) Results of screening for potential candidates from sugars and synthesis gas. In: Werpy T, Petersen G (eds) Top value-added chemicals from biomass – vol. 1. Pacific Northwest National Laboratory, National Renewable Energy Laboratory and Department of Energy, Washington, DC
21. Bozell JJ, Petersen GR (2010) Technology development for the production of biobased products from biorefinery carbohydrates-the US Department of Energy's "Top 10" revisited. Green Chem 12:539–554. https://doi.org/10.1039/B922014C
22. Gallezot P (2012) Conversion of biomass to selected chemical products. Chem Soc Rev 41:1538–1558. https://doi.org/10.1039/C1CS15147A
23. Langeveld H, Sanders J, Meeusen M (eds) (2010) The biobased economy: biofuels, materials and chemicals in the post-oil era. Earthscan, New York, NY
24. Sudhakar T, Tao L, Michael AG (2018) An overview of biorefinery derived platform chemicals from a cellulose and hemicellulose biorefinery, us environmental protection agency. Clean Technol. Environ Policy 20(7):1615–1630. https://doi.org/10.1007/s10098-018-1568-5
25. Mohammadi M, Najafpour GD, Younesi H, Lahijani P, Uzir MH, Mohamed AR (2011) Bioconversion of synthesis gas to second generation biofuels. A review. Renew Sust Energ Rev 15:4255–4273
26. Quellette A, Rawn D (2014) Journal of organic chemistry – structure, mechanism and synthesis. Elsevier, Amsterdam
27. Wu L, Moteki T, Gokhale AA, Flaherty DW, Toste FD (2016) Production of fuels and chemicals from biomass: condensation reactions and beyond. Chemistry 1:32–58. https://doi.org/10.1016/j.chempr.2016.05.002
28. Methanol Institute-Methanol Market Survey Asia (MMSA) (2020) World supply-demand summary, Jan 2020. Accessed 7 Feb 2020
29. Dalena F, Senatore A, Basile M, Knani S, Basile A, Iulianelli A (2018) Advances in methanol production and utilization, with particular emphasis toward hydrogen generation via membrane reactor technology. Membranes 8:98. https://doi.org/10.3390/membranes8040098
30. Sheldon D (2017) Methanol production – a technical history. Johnson Matthey Technol Rev 61(3):172–182. https://doi.org/10.1595/205651317X695622
31. Bertau M, Offermanns H, Plass L, Schmidt F, Wernicke H-J (2014) Methanol: the basic chemical and energy feedstock of the future. Asinger's vision today. Springer, Berlin. https://doi.org/10.1007/978-3-642-39709-7
32. Olah GA (2005) Angew Chem Int Ed 44(18):2636–2639. https://doi.org/10.1002/anie.200462121
33. Olah GA, Goeppert A, Prakash GKS (2018) Beyond oil and gas: the methanol economy. Wiley-VCH, Weinheim
34. Roode-Gutzmer QI, Kaiser D, Bertau M (2019) Renewable methanol synthesis. Chem Bio Eng Rev 6:209–236. https://doi.org/10.1002/cben.201900012
35. Hobson C, Marques C (2018) Renewable methanol report. Methanol Institute, Washington, DC. http://www.mefco2.eu/news/mapping-out-renewable-methanol-around-the-world.php
36. Straathof AJJ (2014) Transformation of biomass into commodity chemicals using enzymes or cells. Chem Rev 114(3):1871–1908. https://doi.org/10.1021/cr400309c
37. Ge X, Yang L, Sheets JP, Yu Z, Li Y (2014) Biological conversion of methane to liquid fuels: status and opportunities. Biotechnol Adv 32(8):1460–1475. https://doi.org/10.1016/j.biotechadv.2014.09.004

38. Hwang IY, Lee SH, Choi YS, Park SJ, Na JG, Chang IS, Kim C, Kim HC, Kim YH, Lee JW, Lee EY (2014) Biocatalytic conversion of methane to methanol as a key step for development of methane-based biorefineries. J Microbiol Biotechnol 24(12):1597–1605. https://doi.org/10.4014/jmb.1407.07070
39. Duan C, Luo M, Xing X (2011) High-rate conversion of methane to methanol by Methylosinus trichosporium OB3b. Bioresour Technol 102(15):7349–7353. https://doi.org/10.1016/j.biortech.2011.04.096
40. Chandran K (2012) Methods and systems for biologically producing methanol. WO 2012/078845 A1
41. Tyurin M, Kiriukhin M (2013) Selective methanol or formate production during continuous CO2 fermentation by the acetogen biocatalysts engineered via integration of synthetic pathways using Tn7-tool. World J Microbiol Biotechnol 29(9):1611–1623. https://doi.org/10.1007/s11274-013-1324-2
42. Johnson D (2012) Global methanol market review. http://www.ptq.pemex.com/productosyservicios/eventosdescargas/Documents/Foro%20PEMEX%20Petroqu%C3%ADmica/2012/PEMEX_DJohnson.pdf. Accessed 23 Mar 2016
43. Rosillo-Calle F, Walter A (2006) Global market for bioethanol: historical trends and future prospects. Energy Sustain Dev 10(1):20–32. https://doi.org/10.1016/s0973-0826(08)605049
44. Kosaric N, Duvnjak Z, Farkas A, Sahm H, Bringer-Meyer S, Goebel O, Mayer D (2011) Ethanol. Ullmann's encyclopedia of industrial chemistry. doi:https://doi.org/10.1002/14356007.a09_587.pu-2
45. Mussatto SI, Dragone G, Guimaraes PM, Silva JP, Carneiro LM, Roberto IC, Vicente A, Domingues L, Teixeira JA (2010) Technological trends, global market, and challenges of bio-ethanol production. Biotechnol Adv 28(6):817–830. https://doi.org/10.1016/j.biotechadv.2010.07.001
46. Demirbas¸ A (2005) Bioethanol from cellulosic materials: a renewable motor fuel from biomass. Energy Sources 27(4):327–337. https://doi.org/10.1080/00908310390266643
47. Ralph EH, Sims WM, Saddler JN, Taylor M (2010) An overview of second generation biofuel technologies. Bioresour Technol 101:1570–1580. https://doi.org/10.1016/j.biortech.2009.11.046
48. Robak K, Balcerek M (2018) Review of second generation bioethanol production from residual biomass. Food Tech BioTech 56(2):174–187. https://doi.org/10.17113/ftb.56.02.18.5428
49. Alalwan AA, Alminshid AH, Aljaafari HAS (2019) Promising evolution of biofuel generations. Subject review. Renew Energy Focus 28:127–139. https://doi.org/10.1016/j.ref.2018.12.006
50. Abdullah B, Muhammad SAFS, Shokravic Z, Ismail S, Kassime KA, Mahmood AN, Azize MMA (2019) Fourth generation biofuel: a review on risks and mitigation strategies. Renew Sust Energ Rev 107:37–50. https://doi.org/10.1016/j.rser.2019.02.018
51. Li K, Liu S, Liu X (2014) An overview of algae bioethanol production. Int J Energy Res 38(8):965–977. https://doi.org/10.1002/er.3164
52. Doutton JA. e-Education Institute, Penn State University, Pennsylvania
53. Rosales-Calderon O, Arantes V (2019) A review on commercial scale high value products that can be produced alongside cellulosic ethanol. Biotechnol Biofuels 12:240. https://doi.org/10.1186/s13068-019-1529-1
54. Bengelsdorf FR, Straub M, Dürre P (2013) Bacterial synthesis gas (syngas) fermentation. Environ Technol 34(13–14):1639–1651. https://doi.org/10.1080/09593330.2013.827747
55. LanzaTech (2015) LanzaTech executive summary. http://www.lanzatech.com/wp-content/uploads/2015/03/2-pager-2015.pdf. Accessed 1 Feb 2017
56. Kuhz H, Kuenz A, Preuße U, Willke T, Vorlop (2017) K-D Products components. Alcohols Adv Biochem Eng Biotechnol 2017:1–34. https://doi.org/10.1007/10_2016_74
57. Papa AJ (2011) Propanols. Ullmann's encyclopedia of industrial chemistry. doi:https://doi.org/10.1002/14356007.a22_173.pub2

58. Ammar EM, Wang Z, Yang ST (2013) Metabolic engineering of Propionibacterium freudenreichii for n-propanol production. Appl Microbiol Biotechnol 97(10):4677–4690. https://doi.org/10.1007/s00253-013-4861-6
59. Choi YJ, Lee J, Jang YS, Lee SY (2014) Metabolic engineering of microorganisms for the production of higher alcohols. MBio 5(5):e01524–e01514. https://doi.org/10.1128/mBio.01524-14
60. Jang YS, Kim B, Shin JH, Choi YJ, Choi S, Song CW, Lee J, Park HG, Lee SY (2012) Bio-based production of C2-C6 platform chemicals. Biotechnol Bioeng 109(10):2437–2459. https://doi.org/10.1002/bit.24599
61. Inokuma K, Liao JC, Okamoto M, Hanai T (2010) Improvement of isopropanol production by metabolically engineered Escherichia coli using gas stripping. J Biosci Bioeng 110(6):696–701. https://doi.org/10.1016/j.jbiosc.2010.07.010
62. Sada M et al (1981) US patent 4307257, 22 Dec 1981
63. Harvey BG, Meylemans HA (2011) The role of butanol in the development of sustainable fuel technologies. J Chem Technol Biotechnol 86:2–9. https://doi.org/10.1002/jctb.2540
64. Xue C, Zhao XQ, Liu CG, Chen LJ, Bai FW (2013) Prospective and development of butanol as an advanced biofuel. Biotechnol Adv 31:1575–1584. https://doi.org/10.1016/j.biotechadv.2013.08.004
65. Gautam M, Martin DW (2000) Combustion characteristics of higher-alcohol/gasoline blends. Proc Inst Mech Eng A J Power Energy 214:497–511. doi:10.1243%2F0957650001538047
66. Thompson R, Behnam M, Swana J, Yang Y (2011) An analysis of net energy production and feed-stock availability for biobutanol and bioethanol. Bioresour Technol 102:2112–2117. https://doi.org/10.1016/j.biortech.2010.08.051
67. Singh SB, Dhar A, Agarwal AK (2015) Technical feasibility study of butanol as gasoline blends for powering medium-duty transportation spark ignition engine. Renew Energy 76:706–716. https://doi.org/10.1016/j.renene.2014.11.095
68. Derre P (2007) Biotechnol J Rep 2:1525–1534
69. Ndaba B, Chiyanzu I, Marx S (2015) n-Butanol derived from biochemical and chemical routes: a review. Biotechnol Rep 8:1–9. https://doi.org/10.1016/j.btre.2015.08.001
70. n-Butanol market by application (butyl acrylate, butyl acetate, glycol ethers, direct solvents, plasticizers), and region (Asia Pacific, North America, Europe, Middle East & Africa, South America)—Global Forecast to 2022: a report (CH1543) 2018
71. Hahn HD, Dambkes G, Rupprich N, Bahl H, Frey GD (2013) Butanols. Ullmann's encyclopedia of industrial chemistry. doi:10.1002/14356007.a04_463.pub3
72. Spivey JJ, Groppi G, Cristiani C, Forzatti P (1997) Preparation and characterization of hexaaluminate materials for high-temperature catalytic combustion. Catalysis 13:209. https://doi.org/10.1039/9781847553256
73. Guerbet MCR (1899) Acad Sci Paris 128:1002–1004
74. Guerbet MCR (1909) Acad Sci Paris 149:129–132
75. Kozlowski J T, Davis RJ (2013) Heterogeneous catalysts for the Guerbet coupling of alcohols. ACS Catal 3:1588–1600. https://pubs.acs.org/doi/10.1021/cs400292f
76. Aitchison H, Wingad RL, Wass DF (2016) Homogeneous ethanol to butanol catalysis. ACS Catal Guerbet Renewed 6:7125–7132. https://doi.org/10.1021/acscatal.6b01883
77. Wu X, Fang G, Tong Y, Jiang D, Liang Z, Leng W, Liu L, Tu P, Wang H, Ni J, Li X (2018) Catalytic upgrading of ethanol to n-butanol: progress in catalyst development. ChemSusChem 11:71–85. https://doi.org/10.1002/cssc.201701590
78. Dowson GRM, Haddow MF, Lee J, Wingad RL, Wass DF (2013) Catalytic conversion of ethanol into an advanced biofuel: unprecedented selectivity for n-butanol. Angew Chem Int Ed 52:9005–9008. https://doi.org/10.1002/anie.201303723
79. Jang YS, Malaviya A, Cho C, Lee J, Lee SY (2012) Butanol production from renewable biomass by Clostridia. Bioresour Technol 123:653–663. https://doi.org/10.1016/j.biortech.2012.07.104

80. Garncarek Z, Kociolek-Balawejder E (2009) Biobutanol. Perspectives of the production development. Przem Chem 88(6):658–666
81. Li J, Baral N, Jha A (2014) Acetone–butanol–ethanol fermentation of corn stover by Clostridium species: present status and future perspectives. World J Microbiol Biotechnol 30(4):1145–1157. https://doi.org/10.1007/s11274-013-1542-7
82. Jain S, Yadav MK, Kumar A (2014) In: Babu V, Thapliyal A, Patel GK (eds) Production of butanol: a biofuel in biofuels production. Scrivener Publishing LLC, Beverly, MA, pp 255–284
83. Rathour RK, Ahuja V, Bhatia RK, Bhatt AK (2018) Biobutanol: new era of biofuels. Int J Energy Res 2018:1–14. https://doi.org/10.1002/er.4180
84. Kolesinska B, Fraczyk J, Binczarski M, Modelska M, Berlowska J, Dziugan P, Hubert Antolak H, Kaminski ZJ, Witonska IA, Kregiel D (2019) Butanol synthesis routes for biofuel production: trends and perspectives. Materials 12:350. https://doi.org/10.3390/ma12030350
85. Ezeji T, Groberg M, Qureshi N, Blaschek HP (2003) Continuous production of butanol from starch-based packing peanuts. Appl Biochem Biotechnol 105–108:375–382. https://doi.org/10.1385/abab:106:1-3:375
86. https://www.plasticsinsight.com/resin-intelligence/resin-prices/mono-ethylene-glycolmeg. Accessed on 16th Feb 2020
87. Bio PET (2020) Market size, share, forecast, industry report. Plastics industry. Radiant Insights Inc, San Francisco, CA
88. Sullivan CJ, Anja K, Vorlop K, Dieter (2018) Propanediols. In: Ullmann's encyclopedia of industrial chemistry. Wiley, Weinheim. https://doi.org/10.1002/14356007.a22_163.pub23
89. Alain C, Gilles L (1989) Petrochemical processes. Volume 2: major oxygenated, chlorinated and nitrated derivatives. Editions Technip, New York, NY, p 26. ISBN:9782710805632
90. Feng J, Xu B (2014) Reaction mechanisms for the heterogeneous hydrogenolysis of biomass derived glycerol to propanediols. Prog React Kinet Mech 39:1–15. https://doi.org/10.3184/97809059274714x13874723178485
91. Zheng Y, Chen X, Shen Y (2008) Commodity chemicals derived from glycerol, an Important biorefinery feedstock. Chem Rev 108:5253–5277. https://doi.org/10.1021/cr068216s
92. Ruppert AM, Weinberg K, Palkovits R (2012) Hydrogenolysis goes bio: from carbohydrates and sugar alcohols to platform chemicals. Angew Chem 51:2564–2601. https://doi.org/10.1002/anie.201105125
93. Nakamura CE, Whited GM (2003) Metabolic engineering for the microbial production of 1,3-propanediol. Curr Opin Biotechnol 14: 454–459. https://www.ncbi.nlm.nih.gov/pubmed/14580573
94. Saxena RK, Anand P, Saran S, Isar J, Agarwal L (2010) Microbial production and applications of 1,2-propanediol. Indian J Microbiol 50:2–11. https://doi.org/10.1007/s12088-010-0017-x
95. Behr A, Eilting J, Irawadi K, Leschinski J, Lindner F (2008) Improved utilisation of renewable resources: new important derivatives of glycerol. Green Chem 10:13. https://doi.org/10.1039/b710561d
96. Zhou CH, Beltramini JN, Fan YX, Lu GQ (2008) Chemo selective catalytic conversion of glycerol as a bio-renewable source to valuable commodity chemicals. Chem Soc Rev 37:527–549. https://doi.org/10.1039/b707343g
97. Pagliaro M, Rossi M (2010) The future of glycerol, vol 2. RSC Green Chemistry Series Royal Society of Chemistry, London
98. Nakagawa Y, Tomishige K (2011) Heterogeneous catalysis of the glycerol hydrogenolysis. Cat Sci Technol 1:179. https://doi.org/10.1039/c0cy00054j
99. Lee CS, Aroua MK, Daud WMAW, Cognet P, Pe're's-Lucchese Y, Fabre PL, Reynes O, Latapie L (2015) A review: conversion of bio-glycerol into 1,3-propanediol via biological and chemical method. Renew Sust Energ Rev 42:963–972. 10.1016/j.rser.2014.10.033
100. Arundhathi R, Mizugaki T, Mitsudome T, Jitsukawa K, Kaneda K (2013) Highly selective hydrogenolysis of glycerol to 1,3-propanediol over a boehmite-supported platinum/tungsten catalyst. ChemSusChem 6(8):1345–1347. https://doi.org/10.1002/cssc.201300196

101. Martin A, Armbruster U, Gandarias I, Arias PL (2013) Glycerol hydrogenolysis into propanediols using in situ generated hydrogen – a critical review. Eur J Lipid Sci Technol 115:9–27. https://doi.org/10.1002/ejlt.201200207
102. Chaminand J, La D, Gallezot P, Marion P, Pinel C, Cc R (2004) Glycerol hydrogenolysis on heterogeneous catalysts. Green Chem 6(8):359. https://doi.org/10.1039/b407378a
103. Ji XJ, Huang H (2014) Bio-based butanediols production: the contributions of catalysis, metabolic engineering, and synthetic biology. In: Bisaria VS, Kondo A (eds) Bioprocessing of renewable resources to commodity bioproducts. Wiley, Hoboken, NJ, pp 261–288
104. Zeng AP, Sabra W (2011) Microbial production of diols as platform chemicals: recent progresses. Curr Opin Biotechnol 22(6):749–757. https://doi.org/10.1016/j.copbio.2011.05.005
105. Grafje H, K€ornig W, Weitz HM, Reiß W, Steffan G, Diehl H, Bosche H, Schneider K, Kieczka H (2000) Butanediols, butenediol, and butynediol. In: Ullmann's encyclopedia of industrial chemistry. https://doi.org/10.1002/14356007.a04_455
106. Bartowsky EJ, Henschke PA (2004) The 'buttery' attribute of wine – diacetyl desirability, spoilage and beyond. Int J Food Microbiol 96(3):235–252. https://doi.org/10.1016/j.ijfoodmicro.2004.05.013
107. Petrini P, Ponti SD, Fare S, Tanzi MC (1999) Polyurethane-maleamides for cardio-vascular applications: synthesis and properties. J Mater Sci Mater Med 10:711–714. https://doi.org/10.1023/A:1008970904334
108. Myszkowski J, Zielinski AZ (1965) Synthe'se de la butyle'ne-chlorhydrine et sa conversion enme'thyle'thylce'tone, oxyde de butyle'ne et butyle'ne-glycol. Chim Ind 93:3
109. Celinska E, Grajek W (2009) Biotechnological production of 2,3-butanediol – current state and prospects. Biotechnol Adv 27:715–725. https://doi.org/10.1016/j.biotechadv.2009.05.002
110. Harden A, Walpole GS (1906) Chemical action of Bacillus lactis aerogenes (Escherich) on glucose and mannitol: production of 2, 3-butyleneglycol and acetyl methyl carbinol. Proc Royal Soc B Bio 77:399–405. https://doi.org/10.1098/rspb.1906.0028
111. Fulmer EI, Christensen LM, Kendali AR (1933) Production of 2,3-butylene glycol by fermentation. Ind Eng Chem 25:798–800. https://doi.org/10.1021/ie50283a019
112. Ji XJ, Huang H, Ouyang PK (2011) Microbial 2,3-butanediol production: a state-of-the art review. Biotechnol Adv 29:351–364. https://doi.org/10.1016/j.biotechadv.2011.01.007
113. Sampat BG (2011) 1,4-Butanediol: a techno-commercial profile. Chem Weekly 2011:205–211
114. Burk MJ (2010) Sustainable production of industrial chemicals from sugars. Int Sugar J 112 (1333):30–35 https://www.genomatica.com/_uploads/pdfs/ISJ_markburke.pdf
115. Burk MJ, Van Dien SJ, Burgard AP, Niu W (2015) Composition and methods for the biosynthesis of 1,4-butanediol and its precursors. US 8969054 B2
116. Genomatica (2015) Commercial-scale production, customer validation, licenses. http://www.genomatica.com/products/genobdoprocess/. Accessed 14 Apr 2015
117. Dittmeyer R, Keim W, Kreysa G, Oberholz A (2005) Chem Tech Prozesse Prod 5:55–68. https://doc1.bibliothek.li/aao/FLMA135383.pdf
118. O'Lenick AJ (2001) Guerbet chemistry. J Surfactant Deterg 4:311–315. https://doi.org/10.1007/s11743-001-0185-1
119. Ott J, Gronemann V, Pontzen F, Fiedler E, Grossmann G, Kersebohm DB, Weiss G, Witte C (2012) Methanol. Ullmann's encyclopedia of industrial chemistry. doi:https://doi.org/10.1002/14356007.a16465.pub3
120. Morschbacker A (2009) Bio-ethanol based ethylene. Polym Rev 49:79–84. https://doi.org/10.1080/15583720902834791
121. Forestie're A, Olivier-Bourbigou H, Saussine L (2009) Oligomerization of mono olefins by homogeneous catalysts. Oil Gas Sci Technol Rev l'IFP 64:649–667. https://doi.org/10.2516/ogst/2009027
122. Olson ES, Sharma RK, Aulich TR (2004) Higher-alcohols biorefinery. Appl Biochem Biotechnol 113–116:913–932. https://doi.org/10.1007/978-1-59259-837-3_74
123. Sun D, Sato S, Ueda W, Primo A, Garcia H, Corma A (2016) Production of C_4 and C_5 alcohols from biomass derived materials. https://doi.org/10.1039/C6GC00377J

124. Luk HT, Mondelli C, CurullaFerre D, Stewart JA, Pe’rez-Ramı’rez J (2017) Status and prospects in higher alcohols synthesis from syngas. Chem Soc Rev 46:1358–1426. https://doi.org/10.1039/c6cs00324a
125. Nexant Inc. (2015) Petrochemical market dynamics oxo alcohols. Nexant Inc., Louisville, CO
126. Lamsen EN, Atsumi S (2012) Recent progress in synthetic biology for microbial production of C3-C10 alcohols. Front Microbiol 3:196. https://doi.org/10.3389/fmicb.2012.00196
127. Zhao J, Lu C, Chen C-C, Yang S-T (2013) In: Yang S-T, El-Enshasy HA, Thongchul N (eds) Bioprocessing technologies in biorefinery for sustainable production of fuels, chemicals, and polymers, 1st edn. John Wiley & Sons, Inc., pp 235–261
128. Diender M, Alfons JMS, Sousa DZ (2016) Biotechnol Biofuels 9:82. https://doi.org/10.1186/s13068-016-0495-0
129. Polyols (sugar alcohols) – a global market overview industry experts. Report code: FB007, Jan 2017
130. Moon HJ, Jeya M, Kim IW, Lee JK (2010) Biotechnological production of erythritol and its applications. Appl Microbiol Biotechnol 86:1017–1025. https://doi.org/10.1007/s00253-010-2496-4
131. Zhang J, Li J-BWS-B, Liu Y (2013) Advances in the catalytic production and utilization of sorbitol. Ind Eng Chem Res 52:11799–11815. https://doi.org/10.1021/ie4011854
132. Ghosh S, Sudha ML (2012) A review on polyols: new frontiers for health-based bakery, products. Int J Food Sci Nutr 63:372–379. https://doi.org/10.3109/09637486.2011.627846
133. Tathod A, Kane T, Sanil ES, Dhepe PL (2014) Solid base supported metal catalysts for the oxidation and hydrogenation of sugars. J Mol Catal A Chem 388-389:90–99. https://doi.org/10.1016/j.molcata.2013.09.014
134. May A, Pastore GM, Park YK (1993) Microbial transformation of sucrose and glucose to erythritol, Biotechnol Lett, 15:383–388 https://link.springer.com/article/10.1007/BF00128281
135. Van der Klis F, Gootjes L, van Haveren J, van Es DS, Bitter JH (2015) Selective terminal C–C scission of C5-carbohydrates. Green Chem 17:3900–3909. https://doi.org/10.1039/C5GC01012H
136. Zada B, Chen M, Chen C, Yan L, Xu Q, Li W, Guo Q, Fu Y (2017) Recent advances in catalytic production of sugar alcohols and their applications. Sci China Chem 60:853–859. https://doi.org/10.1007/s11426-017-9067-1
137. Fabre L, Gallezot P, Perrard A (2001) Catal Commun 2:249–253. https://doi.org/10.1016/S1566-7367(01)00042-5
138. Fabre L, Gallezot P, Perrard A (2002) Catalytic hydrogenation of arabinonic acid and lactones to arabitol. J Catal 208:247–254. https://doi.org/10.1006/jcat.2002.3567
139. Dickson D, Hussain A, Kumpf B (2019) The future of petrochemicals: growth surrounded by uncertainty. Deloitte Consulting LLP, London. https://www2.deloitte.com/content/dam/Deloitte/us/Documents/energy-resources/the-future-of-petrochemicals.pdf. Accessed 21 Feb 2020
140. Vora BV, Marker TL, Barger PT, Nilsen HR, Kvisle S, Fuglerud T (1997) Economic route for natural gas conversion to ethylene and propylene. Stud Surf Sci Catal 107:87
141. Kaiser S (1985) U.S. Patent 4,499,327
142. Kaiser SW (1985) Arab J Sci Eng 10:361
143. Lewis JMO (1998) In: Ward JW (ed) Catalysis. Elsevier, Amsterdam, p 199
144. Keil F (1999) Methanol-to-hydrocarbons: process technology. Microporous Mesoporous Mater 29:49–66. https://doi.org/10.1016/S1387-1811(98)00320-5
145. Gregor J, Vermeiren W (2003) Proceedings of the fifth EMEA petrochemicals technology conference, 25–26 Jun Paris, Jun 2003
146. Chen JQ, Bozzano A, Glover B, Fuglerud T, Kvisle S (2005) Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process. Catal Today 106:103–107. https://doi.org/10.1016/j.cattod.2005.07.178

147. Yang M, Fan D, Wei Y, Tian P, Liu Z (2019) Recent progress in methanol- to-olefins (MTO) catalysts. Adv Mater 31(50):1902181. https://doi.org/10.1002/adma.201902181
148. Gogate MR (2019) Methanol-to-olefins process technology: current status and future prospects. Pet Sci Technol 37(5):559–565. https://doi.org/10.1080/10916466.2018.1555589
149. Dahl IM, Kolboe S (1996) On the reaction mechanism for hydrocarbon formation from methanol over SAPO-34: 2. Isotopic labeling studies of the co-reaction of propene and methanol. J Catal 161(1):304–309. https://doi.org/10.1006/jcat.1996.0188
150. Xu, S, Zhi, Y, Han, J, Zhang, W, Wu, X, Sun, T, Wei, Y, Liu, Z, Advances in catalysis for methanol-to-olefins conversion, Adv Catal, 61:38–118 doi:10.1016/bs.acat.2017.10.002 2017
151. Tian P, Wei Y, Ye M, Liu Z (2015) Methanol-to-olefins (MTO): from fundamentals to commercialization. ACS Catal 5(3):1922–1938. https://doi.org/10.1021/acscatal.5b00007
152. Chang CD (1984) Methanol conversion to light olefins. Catal Rev Sci Eng 26(3–4):323–344. https://doi.org/10.1080/01614948408064716
153. Koempel, H, Liebner, W (2007) Lurgi's methanol to propylene (MTP®), report on a successful commercialisation, in Natural gas conversion VIII F.B. Noronha, Schmal M, EF Sousa-Aguiar Amsterdam, Elsevier.V:262–267
154. Streb S, Göhna H (2000) Mega methanol. Paving the way for new downstream industries. World methanol conference, Copenhagen, 8–10 Nov 2000
155. Rothaemel M, Holtmann HD (2001) MTP, methanol to propylene – Lurgi's way, DGMK-conference "creating value from light olefins – production and conversion, Hamburg, 10–12 Oct 2001
156. Rothaemel M (2016) Methanol-to-propylene (MTP®): a proven technology for on-purpose propylene production NGCS 11 conference, Tromso, Norway, 6–9 Jun. doi:10.13140/RG.2.2.31772.49283
157. Jasper S, Mahmoud M, El-Halwagi A (2015) Techno-economic comparison between two methanol-to-propylene processes. PRO 3:684–698. https://doi.org/10.3390/pr3030684
158. Amghizar I, Laurien A, Vandewalle KM, Van Geem Guy MB (2017) New trends in olefin production. Engineering 3:171–178. https://doi.org/10.1016/J.ENG.2017.02.006
159. Adkins H, Perkins PP (1925) Dehydration of alcohol over alumina. J Am Chem Soc 47:1163–1167. https://doi.org/10.1021/ja01681a036
160. Kochar NK, Merims R, Padia AS (1981) Ethylene from ethanol. Chem Eng Prog 6:66–70
161. Fathi-Afshar F, Rudd DF (1980) Biomass ethanol as a chemical feedstock in the United States. Biotechnol Bioeng XXII:677–679
162. Fan D, Dai D-J, Wu H-S (2013) Ethylene formation by catalytic dehydration of ethanol with industrial considerations. Materials 6:101–115. https://doi.org/10.3390/ma6010101
163. Tsao U, Zasloff H.B (1979) Production of ethylene from ethanol, US patent, 4134926A
164. Mohsenzadeh A, Zamani A, Mohammad TJ (2017) Bio-ethylene production from ethanol: a review and techno-economical evaluation. Chem Bio Eng Rev 4:1–18. https://doi.org/10.1002/cben.201600025
165. Hulea V (2018) Toward platform chemicals from bio-based ethylene: heterogeneous catalysts and processes. ACS Catal 8:3263––327. https://doi.org/10.1021/acscatal.7b04294
166. Sun J, Wang Y (2014) Recent advances in catalytic conversion of ethanol to chemicals. ACS Catal 4:1078–1090. https://doi.org/10.1021/cs4011343
167. Al-Ali AlMa'adeed M, Krupa I (2016) Polyolefin compounds and materials: fundamentals and industrial applications. Springer, Berlin
168. Al-Jarallah AM, Anabtawi JA, Siddiqui MAB, Aitani AM, Alsa'doun AW (1992) Part 1 dimerization of ethylene to butene-1. Catal Today 14:1––121. https://doi.org/10.1016/0920-5861(92)80128-A
169. McGuinness DS (2011) Olefin oligomerization via metallacycles: dimerization, trimerization, tetramerization, and beyond. Chem Rev 111:2321–2341. https://doi.org/10.1021/cr100217q

170. Olivier-Bourbigou H, Forestière A, Saussine L, Magna L, Favre F, Hugues F (2010) Olefin oligomerization for the production of fuels and petrochemicals. Oil Gas Eur Mag, 36:97−102. https://www.osti.gov/etdeweb/biblio/21327984
171. Svejda SA, Brookhart M (1999) Ethylene oligomerization and propylene dimerization using cationic (α-diimine) nickel(II) catalysts. Organometallics 18:65–74. https://doi.org/10.1021/om980736t
172. Finiels A, Fajula F, Hulea V (2014) Nickel-based solid catalysts for ethylene oligomerization. A review. Cat Sci Technol 4:2412–2426. https://doi.org/10.1039/C4CY00305E
173. Skupinska J (1991) Oligomerization of alpha-olefins to higher oligomers. Chem Rev 91:613–648. https://doi.org/10.1021/cr00004a007
174. Andrei RD, Popa MI, Fajula F, Hulea V (2015) Heterogeneous oligomerization of ethylene over highly active and stable Ni-AlSBA-15 mesoporous catalysts. J Catal 323:76––84. https://doi.org/10.1016/j.jcat.2014.12.027
175. Agirrezabal-Telleria I, Iglesia E (2017) Stabilization of active, selective, and regenerable Ni-based dimerization catalysts by condensation of ethene within ordered mesopores. J Catal 352:505–514. https://doi.org/10.1016/j.jcat.2017.06.025
176. Mol JC (2004) Industrial applications of olefin metathesis. J Mol Catal A Chem 213:39––45. https://doi.org/10.1016/j.molcata.2003.10.049
177. Lwin S, Wachs IE (2014) Olefin metathesis by supported metal oxide catalysts. ACS Catal 4:2505–2520. https://doi.org/10.1021/cs500528h
178. Andrei RD, Popa MI, Cammarano C, Hulea V (2016) Nickel and molybdenum containing mesoporous catalysts for ethylene oligomerization and metathesis. New J Chem 40:4146–4152. https://doi.org/10.1039/C5NJ02586A
179. Andrei RD, Popa MI, Fajula F, Cammarano C, AlKhudhair A, Bouchmella K, Mutin PH, Hulea V (2015) Ethylene to propylene by one-pot catalytic cascade reactions. ACS Catal 5:2774–2777. https://doi.org/10.1021/acscatal.5b00383
180. Lin B, Zhang Q, Wang Y (2009) Catalytic conversion of ethylene to propylene and butenes over H-ZSM-5. Ind Eng Chem Res 48:10788−10795. https://doi.org/10.1021/ie901227p
181. Oikawa H, Shibata Y, Inazu K, Iwase Y, Murai K, Hyodo S, Kobayashi G, Baba T (2006) Highly selective conversion of ethylene to propene over SAPO-34 as a solid acid catalyst. Appl Catal A 312:181–185. https://doi.org/10.1016/j.apcata.2006.06.045
182. Song ZX, Takahashi A, Mimura N, Fujitani T (2009) Production of propylene from ethanol over ZSM-5 zeolites. Catal Lett 131:364–369. https://doi.org/10.1007/s10562-009-0071-3
183. Mizuno S, Kurosawa M, Tanaka M, Iwamoto M (2012) One-path and selective conversion ethanol to propene on scandium-modified indium oxide catalysts. Chem Lett 41:892–894. https://doi.org/10.1246/cl.2012.892
184. Iwamoto M (2011) One step formation of propene from ethene or ethanol through metathesis on nickel ion-loaded silica. Molecules 16:7844–7863. https://doi.org/10.3390/molecules16097844
185. Nishiguchi T, Matsumoto T, Kanai H, Utani K, Matsumura Y, Shen WJ, Imamura S (2005) Catalytic steam reforming of ethanol to produce hydrogen and acetone. Appl Catal A 2005(279):273–277. https://doi.org/10.1016/j.apcata.2004.10.035
186. Murthy RS, Patnaik P, Sidheswaran P, Jayamani M (1988) Conversion of ethanol to acetone over promoted iron oxide catalysis. J Catal 109:298–302. https://doi.org/10.1016/0021-9517(88)90212-6
187. Nakajima T, Nameta H, Mishima S, Matsuzaki I, Tanabe KJ (1994) A highly active and highly selective oxide catalyst for the conversion of ethanol to acetone in the presence of water vapour. Mater Chem 4:853––858. https://doi.org/10.1039/JM9940400853
188. Bussi J, Parodi S, Irigaray B, Kieffer R (1998) Catalytic transformation of ethanol into Acetone using copper pyrochlore catalysts. Appl Catal A 172:117–129. https://doi.org/10.1016/S0926-860X(98)00106-9

189. Xu T, Munson EJ, Haw JF (1994) Toward a systematic chemistry of organic reactions in zeolites: in situ NMR studies of ketones. J Am Chem Soc 116:1962–1972. https://doi.org/10.1021/ja00084a041
190. Zaki MI, Hasan MA, Pasupulety L (2001) Surface reactions of acetone on Al_2O_3, TiO_2, ZrO_2, and CeO: IR spectroscopic assessment of impacts of the surface acid−base properties. Langmuir 17:768–774. https://doi.org/10.1021/la000976p
191. Panov AG, Fripiat JJ (1998) Acetone condensation reaction on acid catalysts. J Catal 178:188–197. https://doi.org/10.1006/jcat.1998.2142
192. Hutchings GJ, Johnston P, Lee DF, Warwick A, Williams CD, Wilkinson M (1994) The conversion of methanol and other O-compounds to hydrocarbons over zeolite β. J Catal 147:177–185. https://doi.org/10.1006/jcat.1994.1128
193. Masuda T, Fujikata Y, Mukai SR, Hashimoto K (1998) Changes in catalytic activity of MFI-type zeolites caused by dealumination in a steam atmosphere. Appl Catal A 172:73–83. https://doi.org/10.1016/S0926-860X(98)00120-3
194. Zhu KK, Sun JM, Liu J, Wang LQ, Wan HY, Hu JZ, Wang Y, Peden CHF, Nie ZM (2011) Solvent evaporation assisted preparation of oriented nanocrystalline mesoporous MFI zeolites. ACS Catal 1:682–−690. https://doi.org/10.1021/cs200085e
195. Zhu KK, Sun JM, Zhang H, Liu J, Wang Y (2012) J Nat Gas Chem 21:215–−232
196. Sun J, Zhu K, Gao F, Wang C, Liu J, Peden CHF, Wang YJ (2011) Direct conversion of bio-ethanol to isobutene on nanosized ZnxZryOz mixed oxides with balanced acid-base sites. J Am Chem Soc 133:11096–11099. https://doi.org/10.1021/ja204235v
197. Liu C, Sun J, Smith C, Wang Y (2013) A study of ZnxZryOz mixed oxides for direct conversion of ethanol to isobutene. Appl Catal A 467:91–97. https://doi.org/10.1016/j.apcata.2013.07.011
198. Global Butadiene Market Overview (2020) Prismane consulting. https://www.openpr.com/news/1831666/global-butadiene-market-overview. Accessed 25 Feb 2020
199. Pomalaza G, Capron M, Ordomsky V, Dumeignil V (2016) Recent breakthroughs in the conversion of ethanol to butadiene. Catalysts 6:203. https://doi.org/10.3390/catal6120203
200. Shylesh S, Gokhale AA, Scown CD, Kim D, Christopher R, Ho CR, Bell AT (2016) From sugars to wheels: the conversion of ethanol to 1,3-butadiene over metal-promoted magnesia-silicate, catalysts. ChemSusChem 9:1462–1472. https://doi.org/10.1002/cssc.201600195
201. Lebedev SV (1929) FR 665917
202. Lebedev SV (1930) GB 331482
203. Lebedev SV (1933) Zhurnal Obshchei Khimii 3:698
204. Ostromislenskiy J (1915) J Russ Phys Chem Soc 47:1472–1506
205. Jonathan B, Ross F, Philip L, Peter T (2012) Two-step production 1,3-butadiene from ethanol. Senior Design Rep (CBE) 42. http://repository.upenn.edu/cbe_sdr/42
206. Ezinkwo GO, Tretyakov VP, Aliyu A, Ilolov AM (2014) Fundamental issues of catalytic conversion of bio-ethanol into butadiene. Chem Bio Eng Rev 1:194–203. https://doi.org/10.1002/cben.201400007
207. Makshina EV, Dusselier M, Janssens W, Degrève J, Jacobs PA, Sels BF (2014) Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene. Chem Soc Rev 43:7917–7953. https://doi.org/10.1039/C4CS00105B
208. Angelici C, Weckhuysen BM, Bruijnincx PCA (2013) Chemo catalytic conversion of ethanol into butadiene and other bulk chemicals. ChemSusChem 6:1595–1614. https://doi.org/10.1002/cssc.201300214
209. Jones M (2014) Catalytic transformation of ethanol into 1,3-butadiene. Chem Cent J 8:53. https://doi.org/10.1186/s13065-014-0053-4
210. Jones M, Keir C, Iulio C, Robertson R, Williams C, Apperley D (2011) Investigations into the conversion of ethanol into 1,3-butadiene. Cat Sci Technol 1:267–272. https://doi.org/10.1039/C0CY00081G
211. Kagan MY, Lyubarskii GD, Podurovskaya OM, Izv Akad (1947) Nauk SSSR, Ser Khim, pp 173–181

212. Vinogradova OM, Keier NP, Roginskii SZ (1957) Dokl. Akad Nauk SSSR 112:1075–1078
213. Toussaint WJ, Dunn JT (1947) US 2,421,361
214. Toussaint W.J, Dunn J. T, Jackson D. R (1947) Ind Eng Chem, 39, 120–125. https://pubs.acs.org/doi/pdf/10.1021/ie50446a010
215. Delacaillerie JBD, Gruver V, Fripiat JJ (1995) Modification of the surface properties of natural phyllosilicate sepiolite by secondary isomorphic substitution. J Catal 151:420–430. https://doi.org/10.1006/jcat.1995.1044
216. Gruver V, Sun A, Fripiat J. J, (1995) Catalytic properties of aluminated sepiolite in ethanol conversion. Catal Lett 34:359–364. https://link.springer.com/article/10.1007/BF00806885
217. Chieregato A, Ochoa JV, Cavani F (2016) Olefins from biomass. In: Chemicals and fuels from bio-based building blocks. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, pp 1–32
218. Natta G, Rigamonti R (1947) Chim Ind 29:95
219. Corson, B. B, Jones H.E, Welling C.E, Hinckley J.A, Stahly E.E (1950) Butadiene from ethyl alcohol, Ind Eng Chem, 42:359. https://pubs.acs.org/doi/pdf/10.1021/ie50482a039
220. Kitayama Y, Michishita A (1981) Catalytic activity of fibrous clay mineral sepiolite for butadiene formation from ethanol. J Chem Soc Chem Commun 9:401–402. https://doi.org/10.1039/C39810000401
221. Kitayama Y, Satoh M, Kodama, T (1996) Preparation of large surface area nickel magnesium silicate and its catalytic activity for conversion of ethanol into buta-1,3-diene Catal Lett36:95 https://link.springer.com/article/10.1007/BF00807211
222. Ohnishi R, Akimoto T, Tanabe K (1985) Pronounced catalytic activity and selectivity of MgO–SiO_2–Na_2O for synthesis of buta-1,3-diene from ethanol. J Chem Soc Chem Commun 22:1613–1614. https://doi.org/10.1039/C39850001613
223. Kvisle S, Aguero A, Sneeden RPA (1988) Transformation of ethanol into 1,3-butadiene over magnesium oxide/silica catalysts. Appl Catal 43:117–131. https://doi.org/10.1016/S0166-9834(00)80905-7
224. Makshina EV, Janssens W, Sels BF, Jacobs PA (2012) Catalytic study of the conversion of ethanol into 1,3-butadiene. Catal Today 198:338–344. https://doi.org/10.1016/j.cattod.2012.05.031
225. Bhattacharyya, S, K, Ganguly, N. D (1962) One-step catalytic conversion of ethanol to butadiene in the fixed bed. II binary- and ternary-oxide catalysts J Appl Chem, 12:105–110. https://doi.org/10.1002/jctb.5010120302
226. Bhattacharyya, S. K, Avasthi, B. N (1963) One-step catalytic conversion of ethanol to Butadiene in a fluidized bed, Ind Eng Chem Process Des Dev, 2, 45–51. https://pubs.acs.org/doi/pdf/10.1021/i260005a010
227. Chung SH, Angelici C, Hinterding SOM, Weingarth M, Baldus M, Houben K, Weckhuysen M, Bruijnincx PCA (2016) On the role of magnesium silicates in wet-kneaded silica-magnesia catalysts for the Lebedev ethanol-to-butadiene process. ACS Catal 6:4034–4045. https://doi.org/10.1021/acscatal.5b02972
228. Angelici C, Velthoen MEZ, Weckhuyse BM, Bruijnincx PCA (2015) Influence of acid– base properties on the Lebedev ethanol-to-butadiene process catalyzed by SiO_2 – MgO materials. Cat Sci Technol 5:2869–2879. https://doi.org/10.1039/C5CY00200A
229. Patel AD, Meesters K, den Uil H, de Jong E, Blok K, Patel MK (2012) Sustainability assessment of novel chemical processes at early stage: application to biobased processes. Energy Environ Sci 5:8430. https://doi.org/10.1039/c2ee21581k
230. Chang CD, Silvestri AJ (1977) The conversion of methanol and other o-compounds to hydrocarbons over zeolite catalysts. J Catal 47:249–259
231. Derouane EG, Nagy JB, Dejaifve P, Van hoof JHC, Ben P, Spekman BP, Vedrine JC, Naccache C (1978) Elucidation of the mechanism of conversion of methanol and ethanol to hydrocarbons on a new type of synthetic zeolite. J Catal 53:40–55. https://doi.org/10.1016/0021-9517(78)90006-4

232. Chang CD, Lang W, Smith R (1979) The conversion of methanol and other O- compounds to hydrocarbons over zeolite catalysts: II. Pressure effects. J Catal 56:69–173. https://doi.org/10.1016/0021-9517(79)90103-9
233. Chang, C. D, James, C.W, Kuo, J.C.W, Lang, W.H, Solomon M, Jacob, S.M, Wise, J.J. Silvestri, A. J, (1978) Process studies on the conversion of methanol to gasoline, Ind Eng Chem Process Des Dev, 17, 255–260. https://pubs.acs.org/doi/pdf/10.1021/i260067a008
234. Yurchak S (1988) Development of Mobil's fixed-bed methanol-to-gasoline (MTG) process. Stud Surf Sci Catal 36:251–272. https://doi.org/10.1016/S0167-2991(09)60521-8
235. Tabak S, Yurchak S (1990) Conversion of methanol over ZSM-5 to fuels and chemicals. Catal Today 6:307–327. https://doi.org/10.1016/0920-5861(90)85007-B
236. Tabak S, Heinritz-Adrian M, Brandl A, McGihon R, Brandl A (2008) An alternative route for coal to liquid fuel-applying the exxon mobil methanol to gasoline (MTG) process, gasification technologies conference, 5–8 Oct, Washington, DC
237. Helton T, Hindman M (2014) Methanol to gasoline technology – an alternative for liquid fuel production-GTL technology forum, Texas, USA, 30–31 Jul 2014
238. Udessen H (2013) TIGAS—Topsoe improved gasoline synthesis, 16th IMPCA-2013 Asian methanol conference, 30 Oct to 1 Nov 2013
239. Gal E, Fang H, Qin H, Boyajian G, Li N (2015) Comparison of STG+ with other GTL Technologies. PGE_White-paper-GTL-Comparison-V32. www.primusge.com www.chemwinfo.com. Accessed 29 Feb 2020
240. ID:MRFR/CnM/5385-HCR-March 2020. https://www.marketresearchfuture.com/reports/ethanol-market-7304. Accessed 1 Mar 2020
241. Eagan, N. M, Kumbhalkar M.D, Buchanan, J. S, Dumesic, J. A, Huber, G.W (2019) Chemistries and processes for the conversion of ethanol into middle distillate fuels, Nat Rev Chem, 3, 223–249. https://www.nature.com/articles/s41570–019–0084-4
242. Johansson R, Hruby SL, Rass-Hansen J, Christensen CH (2009) The hydrocarbon pool in ethanol-to-gasoline over HZSM-5 catalysts. Catal Lett 127:127–132. https://doi.org/10.1007/s10562-008-9711-2
243. Aguayo AT, Gayubo AG, Atutxa A, Olazar M, Bilbao J (2002) Kinetic Modelling of the Transformation of Aqueous Ethanol into Hydrocarbons on a HZSM-5 Zeolite. J Ind Eng Chem Res 41:4216––4224. https://doi.org/10.1021/ie001115e
244. Costa E, Uguina A, Aguado J, Hernandez PJ (1985) Ethanol to gasoline process: effect of variables, mechanism, and kinetics. Ind Eng Chem Process Des Dev 1985(24):239–244. https://doi.org/10.1021/i200029a003
245. Talukdar AK, Bhattacharyya KG, Sivasanker S (1997) HZSM-5 catalysed conversion of aqueous ethanol to hydrocarbons. Appl Catal A 148:357––371. https://doi.org/10.1016/S0926-860X(96)00240-2
246. Madeira FF, Ben Tayeb K, Pinard L, Vezin H, Maury S, Cadran N (2012) Ethanol Transformation into hydrocarbons on ZSM-5 zeolites: Influence of Si/Al ratio on catalytic performances and deactivation rate. Study of the radical species role. Appl Catal A 443:171–−180. https://doi.org/10.1016/j.apcata.2012.07.037
247. Gayubo AG, Alonso A, Valle B, Aguayo AT, Olazar M, Bilbao J (2010) Hydrothermal stability of HZSM-5 catalysts modified with Ni for the transformation of bioethanol into hydrocarbons. Fuel 89:3365––3372. https://doi.org/10.1016/j.fuel.2010.03.002
248. Saha SK, Sivasanker S (1992) Influence of Zn- and Ga-doping on the conversion of ethanol to hydrocarbons over ZSM-**5**. Catal Lett 15:413–418. https://doi.org/10.1007/BF00769166
249. Tynjala P, Pakkanen TT, Mustamaki S (1998) Modification of ZSM-5 Zeolite with Trimethyl Phosphite. 2. Catalytic Properties in the Conversion of C1−C4 Alcohols. J Phys Chem B 102:5280–5286. https://doi.org/10.1021/jp9806720
250. Viswanadham N, Saxena SK, Kumar J, Sreenivasulu P, Nandan D (2012) Catalytic performance of nano crystalline H-ZSM-5 in ethanol to gasoline (ETG) reaction. Fuel 95:298–304. https://doi.org/10.1016/j.fuel.2011.08.058

251. https://www.maritime-executive.com/article/transport-uses-25-percent-of-world-energy. Accessed 6 Mar 2020
252. International energy outlook-2016 DOE/EIA-0484(2016) I May 2016 www.eia.gov/forecasts/ieo/pdf/0484(2016).pdf
253. Global bioenergy statistics-2019, World Biofuel Association, p 12
254. Wei-Cheng W, Ling T (2016) Bio-jet fuel conversion technologies. Renew Sust Energ Rev 53:801–822. https://doi.org/10.1016/j.rser.2015.09.016
255. US Energy Information Administration (2015) The flight paths for biojet fuel. US Energy Information Administration, Washington, DC, p 20585. https://www.eia.gov/workingpapers/pdf/flightpaths_biojetffuel.pdf
256. Han GB, Jang JM, Hwei-Ahn M, Jung BH (2019) Recent application of bio-alcohol: bio-jet fuel. Inetch Open. https://doi.org/10.5772/intechopen.89719
257. Harmon L, Hallen R, Lilga MA, Heijstra B, Palou-Rivera I, Handler R (2017) A hybrid catalytic route to fuels from biomass syngas OSTI. GOV. doi:https://doi.org/10.2172/142374
258. Humbird RD, Tao L, Kinchin C, Hsu D, Aden A, Schoen P (2011) Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: dilute-acid pre-treatment and enzymatic hydrolysis of corn stover. Report no. NREL/TP-5100-47764. http://www.nrel.gov/docs/fy11osti/47764.pdf
259. Brooks KP, Snowden-Swan LJ, Jones SB, Butcher MG, Lee GSJ, Anderson DM, Frye JG, Holladay JE, Owen J, Harmon L, Burton F, Palou-Rivera I, Plaza J, Handler R, Shonnard D (2016) Low-carbon aviation fuel through the alcohol to jet pathway. In: Chuck C (ed) Biofuels for aviation: feedstocks, technology and implementation. Academic, Cambridge, MA, p 390
260. Lilga MA (2016) Systems and processes for conversion of ethylene feedstocks to hydrocarbon fuels. WO 2016067032, WO 2016067033 (2016); US9,663,416 (2017)
261. Lilga MA, Frye J, Lee S, Albrecht K (2016) Conversion of 2,3 butane-diol to butadiene, U.S. Patent No. 9:434,569 B2
262. Narula CK, Li Z, Casbeer E, Geiger RA, Szybist JP, Keller M, Davison BH, Theiss T. Direct catalytic upgrading of current dilute alcohol fermentation streams to hydrocarbons for fungible fuels. www.energy.gov-2015/04-biochemical_conversion_davison_0315
263. Wyman CE. Novel vertimass catalyst for conversion of ethanol and other alcohols into fungible gasoline, jet, and diesel fuel blend stocks. https://energy.gov/sites/prod/files/2015/07/f24/wyman_bioenergy_2015
264. Hannon JR. Ethanol conversion to fungible gasoline, diesel, and jet fuel blend stocks and high value chemical coproducts (BTEX). www.energy.gov-sites-files-2017/10-hannon_bioeconomy_2017
265. Wyman CE, Hannon J (2016) R systems and methods for reducing energy consumption in production of ethanol fuel by conversion to hydrocarbon fuels US20160362612A1, 15 Dec, 2016
266. Wyman CE, Hannon JR (2019) Systems and methods for improving yields of hydrocarbon fuels from alcohols, US/2019/00119579A1, 25 Apr 2019
267. Narula, C.K, Li, Z, Casbeer, E.M, Geiger, R. A, Debusk, M.M, Keller, M, Buchanan, M.V, and Davison, B.H, Heterobimetallic zeolite, InV-ZSM-5, enables efficient conversion of biomass derived ethanol to renewable hydrocarbons, Sci Rep, 5, 16039. doi: 10.1038/srep16039
268. Narula CK, Davison BH, Keller M (2017) Zeolitic catalytic conversion of alcohols to hydrocarbons, U.S 9533921, 3 Jan 2017
269. Narula CK, Davison BH (2015) Catalytic conversion of alcohols having at least three carbon Atoms to hydrocarbon blend-stock, U.S. 9181493, 10 Nov 2015
270. Narula CK, Davison BH, Keller M. Catalytic conversion of alcohols to hydrocarbons with low benzene content, U.S. 9278892, 8 Mar, US9434658, 5 Sep 2016
271. Hannon JR. Technoeconomic and life-cycle analysis of single-step catalytic conversion of wet ethanol into fungible fuel blend stocks. www.pnas.org/cgi/doi/10.1073/pnas.1821684116

272. Johnston G 2017 Alcohol to jet-iso-butanol—ICAO seminar on alternate fuels, ICAO Head Quarters, Montreal, 8–9 Feb 2017
273. Matthew WP, Taylor JD. Renewable jet fuel blendstock from iso-butanol, US 8975461, 10th Mar 2015; US Pat. Appl. 2011/0288352, 24 Nov 2011
274. Green car Congress, Dec 19th 2019 – Delta enters off-take agreement with Gevo for 10 million gallons per year of sustainable aviation fuel
275. Wright ME (2012) Biomass to alcohol to jet/diesel-APAN Community. community.apan.org›intelligent-evolution-components-attachments, Aus. Brief, final.pdf
276. Cobalt and the Naval Air Warfare Center team up to produce a renewable jet fuel from bio N-butanol from naval-air-warfare-center-team-up-to-produce-a-renewable-jet-fuel-from-bio-n-butanol-143461676.html. http://www.prnewswire.com/news-releases/cobalt-and-the-
277. Naval Air Warfare Center awards contract to Albemarle for processing Cobalt Technologies bio n-butanol to renewable jet fuel using alcohol-to-jet process – Green car Congress, 20 Mar 2012
278. Michael E, Wright ME, Benjamin GH (2008) Quintana RL Highly Efficient Zirconium-catalyzed Batch Conversion of1-Butene: A New Route to Jet Fuels. Energy Fuel 22:3299–3302. https://doi.org/10.1021/ef800380b
279. Ruddy D, Dagle R Li Z (2019) Liquid fuels via upgrading of indirect liquefaction intermediates. WBS: 2.3.1.100/304/305. www.energy.gov, 2019/03
280. Bradin D 2014 Process for producing renewable jet fuel compositions, WO 2014/008337 Al, 9 Jun
281. Dagle VL, Smith C, Flake AKO, Gray MJ, Ramaswamy KK, Dagle RA (2016) Integrated process for the catalytic conversion of biomass-derived syngas into transportation fuels. Green Chem 18:1880–1891. https://doi.org/10.1039/c5gc02298c
282. Wang W-C, Tao L, Markham J, Zhang Y, Tan E, Batan L, Warner E, Biddy M (2016) Review of biojet fuel conversion technologies, technical report NREL/TP-5100-66291, July. National Renewable Energy Laboratory, Golden, CO. www.nrel.gov/publications
283. Cortright R, Davda R, Dumesic J (2002) Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. Nature 418(6901):964–976. https://doi.org/10.1038/nature01009
284. Davda R, Shabaker J, Huber G, Cortright RJ, Dumesic JA (2005) A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts. Appl Catal B Environ 56:171–186. https://doi.org/10.1016/j.apcatb.2004.04.027
285. Hoang, T. M. C, Vikla, A.K.K Seshan K 2016 Aqueous-phase reforming of sugar derivatives: challenges and opportunities, in Dmitry Murzin and Olga Simakova Biomass sugars for non-fuel applications, RSC Green Chemistry The Royal Society of Chemistry London 44, pp. 54–88
286. Fasolini A, Cucciniello R, Paone E, Mauriello F, Tabanelli TA (2019) Short overview on the hydrogen production via aqueous phase reforming (APR) of cellulose, C_6-C_5 sugars and polyols. Catalysts 9:917. https://doi.org/10.3390/catal9110917
287. Vaidya PD, Lopez-Sanchez JA (2017) Review of hydrogen production by catalytic aqueous-phase reforming. Chem Select 2:6563–6576. https://doi.org/10.1002/slct.201700905
288. Davda R, Shabaker J, Huber G, Cortright RJ, Dumesic JA (2003) Aqueous phase reforming of ethylene glycol on silica-supported metal catalysts. Appl Catal B Environ 43:13–26. https://doi.org/10.1016/S0926-3373(02)00277-1
289. Chen G, Li W, Chen H, Yan B (2015) Progress in the aqueous-phase reforming of different biomass-derived alcohols for hydrogen production. J Zhejiang Univ Sci A (Appl Phys Eng) 16(6):491–506. https://doi.org/10.1631/jzus.A1500023
290. Kim TW, Kim HD, Jeong KE, Chae H-J, Jeong S-Y, Lee C-H, Kim C-U (2011) Catalytic production of hydrogen through aqueous-phase reforming over platinum/ordered mesoporous carbon catalysts. Green Chem 13(7):1718–1728. https://doi.org/10.1039/c1gc15235a

291. Kim HD, Park HJ, Kim TW, Jeong K-E, Chae H-J, Jeong S-Y, Lee C-H, Kim C-U (2012) Hydrogen production through the aqueous phase reforming of ethylene glycol over supported Pt-based bimetallic catalysts. Int J Hydrog Energy 37(10):8310–8317. https://doi.org/10.1016/j.ijhydene.2012.02.160
292. Kim HD, Park HJ, Kim TW, Jeong K-E, Chae H-J, Jeong S-Y, Lee C-H, Kim C-U (2012) The effect of support and reaction conditions on aqueous phase reforming of polyol over supported Pt-Re bimetallic catalysts. Catal Today 185(1):73–80. https://doi.org/10.1016/j.cattod.2011.08.012
293. Huber GW, Shabaker JW, Evans ST, Dumesic JA (2006) Aqueous-phase reforming of ethylene glycol over supported Pt and Pd bimetallic catalysts. Appl Catal B Environ 62:226–235. https://doi.org/10.1016/j.apcatb.2005.07.010
294. Bai Y, Lu CS, Ma L, Chen P, Zheng YF, Li XN (2006) Hydrogen production by aqueous-phase reforming of ethylene glycol over Pt catalysts supported on γ-Al2O3 modified with Ce and Mg. Chin J Catal 27(3):275–280
295. Wawrzetz A, Peng B, Hrabar A, Jentys A, Lemonidou AA, Lercher JA (2010) Towards understanding the bifunctional hydrodeoxygenation and aqueous phase reforming of glycerol. J Catal 269(2):411–420. https://doi.org/10.1016/j.jcat.2009.11.027
296. Barbelli ML, Pompeo F, Santori GF, Nichio NN (2013) Pt catalyst supported on α-Al_2O_3 modified with CeO_2 and ZrO_2 for aqueous-phase-reforming of glycerol. Catal Today 213:58–64. https://doi.org/10.1016/j.cattod.2013.02.023
297. Wen G, Xu Y, Ma H, Xu Z, Tian Z (2008) Production of hydrogen by aqueous-phase reforming of glycerol. Int J Hydrog Energy 33(22):6657–6666. https://doi.org/10.1016/j.ijhydene.2008.07.072
298. Fasolini A, Cespi D, Tabanelli T, Cucciniello R, Cavani F (2019) Hydrogen from renewables: a case study of glycerol reforming. Catalysts 9:722. https://doi.org/10.3390/catal9090722
299. Seretis A, Tsiakaras P (2016) Hydrogenolysis of glycerol to propylene glycol by in situ produced hydrogen from aqueous phase reforming of glycerol over SiO_2– Al_2O_3 supported nickel catalyst. Fuel Process Technol 142:135–146
300. Iriondo A, Barrio VL, Cambra JF, Arias PL, Guemez MB, Navarro RM, Sánchez-Sánchez MC, Fierro JLG (2008) Hydrogen production from glycerol over nickel catalysts supported on Al_2O_3 modified by Mg, Zr, Ce or La. Top Catal 49:46–58. https://doi.org/10.1007/s11244-008-9060-9
301. Haryanto A, Fernando S, Murali N, Adhikari S (2005) Current status of hydrogen production techniques by steam reforming of ethanol: a review. Energy Fuel 19:2098–2106. https://doi.org/10.1021/ef0500538
302. Tokarev A, Kirilin A, Murzina E, Eranen K, Mikkola JP (2010) The role of bio-ethanol in aqueous phase reforming to sustainable hydrogen. Int J Hydrog Energy 35:12642–12649. https://doi.org/10.1016/j.ijhydene.2010.07.118
303. Roy B, Loganathan K, Pham H, Datye AK, Leclerc CA (2010) Surface modification of solution combustion synthesized Ni/Al_2 O_3 catalyst for aqueous-phase reforming of ethanol. Int J Hydrog Energy 35:11700–11708. https://doi.org/10.1016/j.ijhydene.2010.07.167
304. Roy B, Martinez U, Loganathan K, Datye AK, Leclerc CA (2012) Effect of preparation methods on the performance of Ni/Al_2 O_3 catalysts for aqueous-phase reforming of ethanol: Part I catalytic activity. Int J Hydrog Energy 37:8143–8153. https://doi.org/10.1016/j.ijhydene.2012.02.056
305. Roy B, Artyushkova K, Pham H, Li L, Leclerc CA (2012) Effect of preparation method on the performance of the Ni/Al_2O_3 catalysts for aqueous-phase reforming of ethanol: Part II characterization. Int J Hydrog Energy 37:18815–18826. https://doi.org/10.1016/j.ijhydene.2012.09.098
306. Nozawa T, Mizukoshi Y, Yoshida A, Naito S (2014) Aqueous phase reforming of ethanol and acetic acid over TiO2 supported Ru catalysts. Appl Catal B Environ 146:221–226. https://doi.org/10.1016/j.apcatb.2013.06.017

307. Cruz IO, Ribeiro NF, Aranda DA, Souza MMVM (2008) Hydrogen production by aqueous-phase reforming of ethanol over nickel catalysts prepared from hydrotalcite precursors. Catal Commun 9:2606–2611. https://doi.org/10.1016/j.catcom.2008.07.031
308. Roy B, Sullivan H, Leclerc CA (2011) Aqueous-phase reforming of n-BuOH over Ni/Al_2O_3 and Ni/CeO_2 catalysts. J Power Sources 196:10652–10657. https://doi.org/10.1016/j.jpowsour.2011.08.093
309. Shabaker JW, Davda RR, Huber GW, Cartwright RD (2003) Aqueous-phase reforming of methanol and ethylene glycol over alumina-supported platinum catalysts. J Catal 215:344–352. https://doi.org/10.1016/S0021-9517(03)00032-0
310. Liu XH (2011) Aqueous-phase reforming of ethylene glycol to hydrogen on supported platinum catalysts. Ph.D. thesis. East China University of Science and Technology, Shanghai
311. Rose M, Palkovits R (2012) Isosorbide as a renewable platform chemical for versatile applications—quo vadis? ChemSusChem 5:167–176. https://doi.org/10.1002/cssc.201100580
312. Kobayashi H, Fukuoka A (2013) Synthesis and utilisation of sugar compounds derived from lignocellulosic biomass. Green Chem 15:1740–1763. https://doi.org/10.1039/c3gc00060e
313. Grand View Research Inc. (2020) Market research report—isosorbide market size, share and trend analysis. Grand View Research Inc., San Francisco, CA. Accessed 22 Mar 2020
314. Besse V, Auvergne R, Carlotti S, Boutevin G, Otazaghine B, Caillol S, Pascault JP, Boutevin B (2013) Synthesis of isosorbide-based polyurethanes: an isocyanate free method. React Funct Polym 73:588–594. https://doi.org/10.1016/j.reactfunctpolym.2013.01.002
315. Otomo R, Yokoi T, Tatsumi T (2015) Synthesis of isosorbide from sorbitol in water over high-silica aluminosilicate zeolites. Appl Catal A Gen 505:28–35. https://doi.org/10.1016/j.apcata.2015.07.034
316. Shi J, Shan Y, Tian Y, Wan Y, Zheng Y, Feng Y (2016) Hydrophilic sulfonic acid-functionalized micro-bead silica for dehydration of sorbitol to isosorbide. RSC Adv 6:13514–13521. https://doi.org/10.1039/x0xx00000x
317. Yamaguchi A, Sato O, Mimura N, Shirai M (2015) One-pot conversion of cellulose to isosorbide using supported metal catalysts and ion-exchange resin. Catal Commun 67:59–63. https://doi.org/10.1016/j.catcom.2015.04.009
318. Xu Y, Tian Z, Wen G, Xu Z, Qu W, Lin L (2006) Production of CO_x-free hydrogen by alkali enhanced hydrothermal catalytic reforming of biomass-derived alcohols. Chem Lett 35:216–217. https://doi.org/10.1246/cl.2006.216
319. Soetaert W, Buchholz K, Vandamme E (1995) Production of D-mannitol and D-lactic acid by fermentation by Leuconostoc mesenteroides Agro Food Ind Hi Tech, 6: 41–44. https://lib.ugent.be/catalog/pug01:256408
320. Clark IT (1958) Hydrogenolysis of sorbitol. Ind Eng Chem 50:1125–1126. https://doi.org/10.1021/ie50584a026
321. Sun J, Liu H (2011) Selective hydrogenolysis of biomass-derived xylitol to ethylene glycol and propylene glycol on supported Ru catalysts. Green Chem 13:135–142. https://doi.org/10.1039/c0gc00571a
322. Nda-Umar UI, Ramli I, Taufiq-Yap YH, Muhamad EN (2019) An overview of recent research in the conversion of glycerol into biofuels, fuel additives and other bio-based chemicals. Catalysts 9:15. https://doi.org/10.3390/catal9010015
323. Cognet P, Aroua MK (eds) (2020) From glycerol to value-added products. Frontiers Media SA, Lausanne. https://doi.org/10.3389/978-2-88963-577-1
324. Demsash HD, Mohan R (2016) Steam reforming of glycerol to hydrogen over ceria promoted nickel–alumina catalysts. Int J Hydrog Energy 41:22732–22742. https://doi.org/10.1016/j.ijhydene.2016.10.082
325. Menezes AO, Rodrigues MT, Zimmaro A, Borges LE, Fraga MA (2011) Production of renewable hydrogen from aqueous-phase reforming of glycerol over Pt catalysts supported on different oxides. Renew Energy 36:595–599. https://doi.org/10.1016/j.renene.2010.08.004

326. Rahmat N, Abdullah AZ, Mohamed AR (2010) Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: a critical review. Renew Sust Energ Rev 14:987–1000. https://doi.org/10.1016/j.rser.2009.11.010
327. García JI, García-Marín H, Pires E (2014) Glycerol based solvents: synthesis, properties and applications. Green Chem 16:1007–1033. https://doi.org/10.1039/C3GC41857J
328. Usai E, Gualdi E, Solinas V, Battistel E (2010) Simultaneous enzymatic synthesis of FAME and triacetyl glycerol from triglycerides and methyl acetate. Bioresour Technol 101:7707–7712. https://doi.org/10.1016/j.biortech.2010.05.044
329. Morales G, Paniagua M, Melero JA, Vicente G, Ochoa C (2011) Sulfonic acid- functionalized catalysts for the valorization of glycerol via transesterification with methyl acetate. Ind Eng Chem Res 50:5898–5906. https://doi.org/10.1021/ie102357c
330. Silva LN, Gonçalves VL, Mota CJ (2010) Catalytic acetylation of glycerol with acetic anhydride. Catal Commun 11:1036–1039. https://doi.org/10.1016/j.catcom.2010.05.007
331. Gonzalez-Arellano C, De S, Luque R (2014) Selective glycerol transformations to high value-added products catalysed by aluminosilicate-supported iron oxide nanoparticles. Catal Sci Technol 4:4242–4249. https://doi.org/10.1039/C4CY00714J
332. Sandesh S, Kristachar PKR, Manjunathan P, Halgeri AB, Shanbhag GV (2016) Synthesis of biodiesel and acetins by transesterification reactions using novel CaSn $(OH)_6$ heterogeneous base catalyst. Appl Catal A Gen 523:1–11. https://doi.org/10.1016/j.apcata.2016.05.006
333. Gonçalves M, Souza VC, Galhardo TS, Mantovani M, Figueiredo FVC, Mandelli D, Carvalho WA (2013) Glycerol conversion catalyzed by carbons prepared from agro industrial wastes. Ind Engg Chem Res 52:2832–2839. https://doi.org/10.1021/ie303072d
334. Viswanadham N, Saxena SK (2013) Etherification of glycerol for improved production of oxygenates. Fuel 103:980–986. https://doi.org/10.1016/j.fuel.2012.06.057
335. Cornejo A, Barrio I, Campoy M, Lázaro J, Navarrete B (2017) Oxygenated fuel additives from glycerol valorization. Main production pathways and effects on fuel properties and engine performance: a critical review. Renew Sust Energ Rev 79:1400–1413. https://doi.org/10.1016/j.rser.2017.04.005
336. Mota CJ, da Silva CXA, Rosenbach N Jr, Costa J, da Silva FV (2010) Glycerin derivatives as fuel additives: the addition of glycerol/acetone ketal (solketal) in gasolines. Energy Fuel 24:2733–2736. https://doi.org/10.1021/ef9015735
337. Vicente G, Melero JA, Morales G, Paniagua M, Martín E (2010) Acetalization of bio-glycerol with acetone to produce solketal over sulfonic mesostructured silicas. Green Chem 12:899–907. https://doi.org/10.1039/B923681C
338. De Torres M, Jimenez-Oses G, Mayoral JA, Pires E, Santos M (2012) Glycerol ketals: synthesis and profits in biodiesel blends. Fuel 94:614–616. https://doi.org/10.1016/j.fuel.2011.11.062
339. Nanda MR, Yuan Z, Qin W, Ghaziaskar HS, Poirier M-A, Xu CC (2014) A new continuous-flow process for catalytic conversion of glycerol to oxygenated fuel additive: catalyst screening. Appl Energy 123:75–81. https://doi.org/10.1016/j.apenergy.2014.02.055
340. Nanda MR, Yuan Z, Qin W, Ghaziaskar HS, Poirier M-A, Xu CC (2014) Catalytic conversion of glycerol to oxygenated fuel additive in a continuous flow reactor: process optimization. Fuel 128:113–119. https://doi.org/10.1016/j.fuel.2014.02.068
341. Umbarkar SB, Kotbagi TV, Biradar AV, Pasricha R, Chanale J, Dongare MK, Mamede A-S, Lancelot C, Payen E (2009) Acetalization of glycerol using mesoporous MoO_3 /SiO_2 solid acid catalyst. J Mol Catal A Chem 310:150–158
342. Amin T-K, Amin NAS, Najaafi N, Tarighi S (2018) A review on the catalytic acetalization of bio-renewable glycerol to fuel additives. Front Chem 6:573. https://doi.org/10.3389/fchem.2018.00573
343. Ma T, Ding J, Shao R, Xu W, Yun Z (2017) Dehydration of glycerol to acrolein over Wells–Dawson and Keggin type phospho tungstic acids supported on MCM-41 catalysts. Chem Eng J 316: 797–806. http://doi:10.1016/j.cej.2017.02.018
344. Gu Y, Liu S, Li C, Cui Q (2013) Selective conversion of glycerol to acrolein over supported nickel sulfate catalysts. J Catal 301:93–102. https://doi.org/10.1016/j.jcat.2013.01.019

345. Yadav GD, Sharma RV, Katole SO (2013) Selective dehydration of glycerol to acrolein: development of efficient and robust solid acid catalyst MUICaT-5. Ind Eng Chem Res 52:10133–10144. https://doi.org/10.1021/ie401098n
346. Jia C-J, Liu Y, Schmidt W, Lu A-H, Schüth F (2010) Small-sized HZSM-5 zeolite as highly active catalyst for gas phase dehydration of glycerol to acrolein. J Catal 269:71–79. https://doi.org/10.1016/j.jcat.2009.10.017
347. Climent MJ, Corma A, De Frutos P, Iborra S, Noy M, Velty A, Concepción P (2010) Chemicals from biomass: synthesis of glycerol carbonate by transesterification and carbonylation with urea with hydrotalcite catalysts – the role of acid–base pairs. J Catal 269:140–149. https://doi.org/10.1016/j.jcat.2009.11.001
348. Ishak ZI, Sairi NA, Alias Y, Aroua MKT, Yusoff R (2016) Production of glycerol carbonate from glycerol with aid of ionic liquid as catalyst. Chem Eng J 297:128–138. https://doi.org/10.1016/j.cej.2016.03.104
349. Nakagawa Y, Tamura M, Tomishige K (2014) Catalytic materials for the hydrogenolysis of glycerol to 1,3-propanediol. J Mater Chem A 2014(2):6688–6702. https://doi.org/10.1039/c3ta15384c
350. Leoneti AB, Aragão-Leoneti V, De Oliveira SVWB (2012) Glycerol as a by-product of biodiesel production in Brazil: alternatives for the use of unrefined glycerol. Renew Energy 45:138–145. https://doi.org/10.1016/j.renene.2012.02.032
351. Cameron DC, Altaras NE, Hoffman ML, Shaw AJ (1998) Metabolic engineering of propanediol pathways. Biotechnol Prog 14:116–125. https://doi.org/10.1021/bp9701325
352. Gonzalez-Pajuelo M, Meynial-Salles I, Mendes F, Soucaille P, Vasconcelos I (2006) Microbial conversion of glycerol to 1,3-propanediol: physiological comparison of a natural producer, clostridium butyricum VPI 3266, and an engineered strain, clostridium acetobutylicum DG1(pSPD5). Appl Environ Microbiol 72:96–101. https://doi.org/10.1128/AEM.72.1.96-101.2006
353. Gonz'alez-Pajuelo M, Meynial-Salles I, Mendes F, Andrade JC, Vasconcelos I, Soucaille P (2005) Metabolic engineering of *Clostridium acetobutylicum* for the industrial production of 1,3-propanediol from glycerol. Metab Eng 7:329–336. https://doi.org/10.1016/j.ymben.2005.06.001
354. Mu Y, Teng H, Zhang DJ, Wang W, Xiu ZL (2006) Microbial production of 1,3-propanediol by *Klebsiella pneumoniae* using crude glycerol from biodiesel preparations. Biotechnol Lett 28:1755–1759. https://doi.org/10.1007/s10529-006-9154-z
355. Dobson R, Gray V, Rumbold K (2012) Microbial utilization of crude glycerol for the production of value-added products. J Ind Microbiol Biotechnol. https://doi.org/10.1007/s10295-011-1038-0
356. Garlapati VK, Shankar U, Budhiraja A (2016) Bioconversion technologies of crude glycerol to value added industrial products. Biotechnol Rep 9:9–14. https://doi.org/10.1016/j.btre.2015.11.002
357. Mariscal R, Maireles-Torres P, Ojeda M, Sadaba I, Lopez Granados M (2016) Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels. Energy Environ Sci 9:1144–1189. https://doi.org/10.1039/C5EE02666K
358. Wang Y, Zhao, Rodríguez-Padrón D, Len C (2019) Recent advances in catalytic hydrogenation of furfural. Catalysts 9:796. https://doi.org/10.3390/catal9100796
359. Prescient and Strategic Intelligence Pvt. Ltd. Report published in Global Newswire, 7th Nov 2019
360. Bozell JJ, Moens L, Elliot DC, Wang Y, Neuenscwander GG, Fitzpatrick SW, Bilski RJ, Jarnefeld JL (2000) Production of levulinic acid and use as a platform chemical for derived products. Resources, Conservation and Recycling 28:227–239. PII:S0921-3449(99)00047-6
361. Hayes DJ, Fitzpatrick S, Hayes MHB, Ross JRH (2008) The biofine process: production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks. In: Kamm B, Gruber PR, Kamm M (eds) Biorefineries – industrial processes and products. Wiley-VCH, Weinheim

362. Gonzalez Maldonado GM, Assary RS, Dumesic JA, Curtiss LA (2012) Experimental and theoretical studies of the acid-catalyzed conversion of furfuryl alcohol to levulinic acid in aqueous solution. Energy Environ Sci 5:6981–6989. https://doi.org/10.1039/C2EE03465D
363. Xue Z, Liu Q, Wang J, Mu T (2018) Valorization of levulinic acid over non-noble metal catalysts: challenges and opportunities. Green Chem 20:4391–4408. https://doi.org/10.1039/x0xx00000x
364. Ahmad E, Alam MI, Pant KK, Ali Haider M (2018) Catalytic and mechanistic insights into the production of ethyl levulinate from bio renewable feedstocks. Green Chem 18:4804–4823. https://doi.org/10.1039/C6GC01523A
365. Demolis A, Essayem N, Rataboul E (2014) Synthesis and applications of alkyl levulinates. ACS Sust Chem Eng 2:1338–1352. https://doi.org/10.1021/sc500082n
366. Haan RJ, Lange J-P (2011) US Patent Appl., 20110035991A1
367. Haan RJ, Lange J-P (2009) World Patatent, WO 2009077606 A2
368. Lange J-P, Heide E, Buijtenen J, Price R (2012) Furfural-a promising platform for lignocellulosic biofuels. ChemSusChem 5:150–166. https://doi.org/10.1002/cssc.201100648
369. Yang S, Hao Y, Wang J, Wang H, Zheng Y, Tian H, Liu Y, Sun B (2017) Selective catalytic dehydration of furfuryl alcohol to 2,2′-difurfuryl ether using a polyoxometalate catalyst. Sci Rep 7:12954. https://doi.org/10.1038/s41598-017-13472-3
370. Meng Q, Zheng H, Zhu Y, Li Y (2016) Study on the reaction pathway in decarbonylation of biomass-derived 5-hydroxymethylfurfural over Pd-based catalyst. J Mol Catal A Chem 421:76–82. https://doi.org/10.1016/j.molcata.2016.05.012
371. Kim T, Assary RS, Pauls RE, Marshall CL, Curtiss LA, Stair PC (2014) Thermodynamics and reaction pathways of furfuryl alcohol oligomer formation. Catal Commun 46:66–70. https://doi.org/10.1016/j.catcom.2013.11.030
372. Yi B, Rajagopalan R, Foley HC, Kim UJ, Liu X, Eklund PC (2006) Catalytic polymerization and facile grafting of poly (furfuryl alcohol) to single-wall carbon nanotube: preparation of nanocomposite carbon. J Am Chem Soc 128:11307–11313. https://doi.org/10.1021/ja063518x
373. Kumar R, Rajesh A (2012) Process for preparing polyfurfuryl alcohol products, WO 2012/123902 Al, 20 Sep 2012
374. van Buijtenen J, Lange JP, Price RJ (2011) United States Pat., 2011/0173877
375. Moreau C, Belgacem MN, Gandini A (2004) Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers. Top Catal 27:11–30. https://doi.org/10.1023/B:TOCA.0000013537.13540.0e
376. Pranger LA, Nunnery GA, Tannenbaum R (2012) Mechanism of the nanoparticle-catalyzed polymerization of furfuryl alcohol and the thermal and mechanical properties of the resulting nanocomposites. Compos Part B 2012(43):1139–1146. https://doi.org/10.1016/j.compositesb.2011.08.010
377. Takei T, Iguchi N, Haruta M (2010) Synthesis of acetaldehyde, acetic acid, and others by the dehydrogenation and oxidation of ethanol. Catal Surv Jpn 15:80–88. https://doi.org/10.1007/s10563-011-9112-1
378. Gallo JMR, Bueno JMC, Schuchardt U (2014) Catalytic transformations of ethanol for biorefineries. J Braz Chem Soc 25:2229–2243. https://doi.org/10.5935/0103-5053.20140272
379. Pease RN, Yung CC (1924) The catalytic dehydration of ethyl alcohol and ether by alumina. J Am Chem Soc 46:390–340
380. Varisli D, Dogu T, Dogu G (2007) Ethylene and diethyl-ether production by dehydration reaction of ethanol over different heteropoly acid catalysts. Chem Eng Sci 62:5349–5352. https://doi.org/10.1016/j.ces.2007.01.017
381. Sato AG, Volanti DP, de Freitas IC, Longo E, Bueno JMC (2012) Site-selective ethanol conversion over supported copper catalysts. Catal Commun 26:122–126. https://doi.org/10.1016/j.catcom.2012.05.008
382. Obora Y (2014) Recent advances in α-alkylation reactions using alcohols with hydrogen borrowing methodologies. ACS Catal 4:3972–3981. https://doi.org/10.1021/cs501269d

383. Chakraborty S, Daw P, David YB, Milstein D (2018) Manganese-catalyzed α-alkylation of ketones, esters, and amides using alcohols. ACS Catal 8:10300−10305. https://doi.org/10.1021/acscatal.8b03720
384. Chaudhari C, Siddiki SMAH, Kon K, Tomita A, Tai Y, Shimizu K (2014) Cat Sci Technol 4:1064–1069. https://doi.org/10.1039/C3CY00911D
385. Kwon MS, Kim N, Seo SH, Park IS, Cheedrala RK, Park J (2005) Recyclable palladium catalyst for highly selective a alkylation of ketones with alcohols. Angew Chem Int Ed 44:6913–6915. https://doi.org/10.1002/anie.200502422
386. Kwon MS, Kim N, Park CM, Lee JS, Kang KY, Park J (2005) Palladium nanoparticles entrapped in aluminum hydroxide: dual catalyst for alkene hydrogenation and aerobic alcohol oxidation. Org Lett 7:1077–1079. https://doi.org/10.1021/ol047381w
387. Selva M, Perosa A (2008) Green chemistry metrics: comparative evaluation of dimethyl carbonate, methyl iodide, dimethyl sulfate and methanol as methylating agents. Green Chem 10:457–464. https://doi.org/10.1039/B713985C
388. Fu A, Liu Q, Jiang M, Xu G (2019) Selective N-mono methylation of amines and nitroarenes using methanol over an encapsulated iridium nano catalyst. Asian J Org Chem 8:1–6. https://doi.org/10.1002/ajoc.201900140
389. Jiang L, Guo F, Wang Y, Jiang J, Duan Y, Hou Z (2019) Selective *N*-mono methylation of anilines with methanol catalyzed by commercial Pd/C as an efficient and reusable catalyst. Asian J Org Chem 8:1–5. https://doi.org/10.1002/ajoc.201900509
390. Nanda S, Dalai AK, Kozinski JA (2014) Butanol and ethanol production from lignocellulosic feed stock: biomass pretreatment and bioconversion. Energy Sci Eng 2:138–148. https://doi.org/10.1002/ese3.41
391. Bazzanella AM, Ausfelder F (2017) Low carbon energy and feedstock for the European chemical industry. DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V, Frankfurt. ISBN:978-3-89746-196-2
392. Lipinski ES (1981) Chemicals from biomass: petrochemical substitution options. Science 212:1465–1471. https://doi.org/10.1126/science.212.4502.1465
393. Rass-Hansen J, Falsig H, Jørgensen B, Christensen CH (2007) Bio-ethanol: fuel or feedstock? J Chem Technol Biotechnol 82:329. https://doi.org/10.1002/jctb.1665
394. Dale BE, Anderson JE, Brown RC, Csonka S, Dale VH, Herwick G et al (2014) Take a closer look: biofuels can support environmental, economic and social goals. Environ Sci Technol 48:7200–7203. https://doi.org/10.1021/es5025433
395. Balan V, Chiaramonti D, Kumar S (2013) Review of US and EU initiatives toward development, demonstration, and commercialization of lignocellulosic biofuels. Biofuels Bioprod Biorefin 7:732–759. https://doi.org/10.1002/bbb.1436
396. Balan V (2014) Current challenges in commercially producing biofuels from lignocellulosic biomass. Biotechnology 463074:463074. https://doi.org/10.1155/2014/463074
397. Karimi K, Tabatabaei M, Horvath IS, Kumar R (2015) Recent trends in acetone, butanol and ethanol (ABE) production. Biofuel Res J 8:301–308. https://doi.org/10.18331/BRJ2015.2.4.4
398. Biswas S, Katiyar R, Gurjar BR, Pruthi V (2017) Role of different feedstocks on the butanol production through microbial and catalytic routes. Int J Chem Engg 2017:20160215. https://doi.org/10.1515/ijcre-2016-0215
399. Tsvetanova F, Petrova P, Petrov K (2018) Microbial production of 1-butanol – recent advances and future prospects. J Chem Technol Metall 53:683–696. https://www.researchgate.net/publication/325554503
400. Dagle VL, Flake MD, Lemmon TL, Lopez JS, Kovarik L, Dagle RA (2018) Effect of the SiO_2 support on the catalytic performance of $Ag/ZrO_2/SiO_2$ catalysts for the single-bed production of butadiene from ethanol. Appl Catal B Environ 236:576–587. https://doi.org/10.1016/j.apcatb.2018.05.055
401. Cimino S, Lisi L, Romannucci S (2018) Catalysts for conversion of ethanol to butanol: effect of acid-base and redox properties. Catal Today 304:58–63. https://doi.org/10.1016/j.cattod.2017.08.035