



Olefins from Biomass Intermediates: A Review

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Abstract: Over the last decade, increasing demand for olefins and their valuable products has prompted research on novel processes and technologies for their selective production. As olefins are predominately dependent on fossil resources, their production is limited by the finite reserves and the associated economic and environmental concerns. The need for alternative routes for olefin production is imperative in order to meet the exceedingly high demand, worldwide. Biomass is considered a promising alternative feedstock that can be converted into the valuable olefins, among other chemicals and fuels. Through processes such as fermentation, gasification, cracking and deoxygenation, biomass derivatives can be effectively converted into C_2 – C_4 olefins. This short review focuses on the conversion of biomass-derived oxygenates into the most valuable olefins, e.g., ethylene, propylene, and butadiene.

Keywords: olefins; biomass; ethylene; propylene; butadiene; catalysis

1. Introduction

The importance of C_2 – C_4 olefins (i.e., C_2H_4 , C_3H_6 , butenes, and C_4H_6) has been highlighted because of their numerous applications as key building blocks in the chemical industry, linked with the increasing needs of the expanding global population [1]. These lower olefins are the most prevalent organic compounds, with the highest production volumes, worldwide, highly dependent on crude oil and natural gas products [2]. It is estimated that 400 million tons of olefins are annually produced, using one billion tons as hydrocarbon feedstock, via processes such as fluid-catalytic cracking, steam cracking, and dehydrogenation [3]. Almost 60% of the global feedstocks are used in FCC units, and approximately 40% in steam cracking processes. (Figure 1) Produced olefins can be used in a wide spectrum of high-end applications such as packaging, construction, solvents, coatings, and synthetic fibers [4].



Figure 1. Olefin production methods using hydrocarbon feedstocks. Reproduced from [3]. 2014, WILEY-VCH Verlag GmbH & Co.

 C_2H_4 constitutes the most predominant olefin in the global market and is primarily produced via naphtha steam cracking, among various hydrocarbon feedstocks, as well as through ethane thermal cracking. Globally, 57% (Figure 2) of the C_2H_4 volume is produced via naphtha and gas oil steam cracking and 38% through ethane and LPG (Liquefied Petroleum Gas) steam cracking. Naphtha is a liquid fraction obtained from petroleum refining processes, such as catalytic cracking and hydrocracking. Depending on its origin, it contains variable amounts of paraffins, aromatic, and olefinic compounds. The ratio of these components can indicate the process that the specific fraction can be used for the optimum results. At high temperatures (i.e., 650–750 °C), naphtha and gas oil can yield 30 and 25 wt. % of C_2H_4 , respectively. In the case of ethane, added along with naphtha in the feed stream, yields of C_2H_4 can reach 80 wt. % [5]. Its eminent industrial uses cause the world demand for C_2H_4 to increase, as it can be used for significant applications, such as the production of intermediate chemicals, mainly in the industry of plastics. i.e., polymers (e.g., poly-ethylene), propionaldehyde-via hydroformylation, vinyl chloride-via halogenation and de-hydrohalogenation, alpha-olefins—via oligomerization, and C_2H_4 oxide and acetaldehyde—via oxidation [4,6,7]. In recent years, bio-ethanol has been extensively studied as an alternate feedstock for C_2H_4 production [8]. Other bio-derived compounds such as methanol and dimethyl-ether, can also be used as a feedstock for C_2H_4 , via Methanol to Olefins (MTO) and Dimethyl-ether to Olefins (DMTO) processes [9,10]. Bio-ethylene can also be produced via bio-synthesis from various enzymes or microorganisms [11].



Figure 2. C₂H₄ production methods using hydrocarbon feedstocks. Reproduced from [3]. 2014, WILEY-VCH Verlag GmbH & Co.

 C_3H_6 is the second most significant olefin, conventionally produced via steam cracking, as a co-product, or through fluid catalytic cracking (FCC). (Figure 3) C_2H_4 and gasoline production severely affect C_3H_6 production; recently, steam crackers switch to ethane feedstocks, suppressing concurrent production of C_3H_6 , while its demand outpaces existing steam and fluid catalytic cracking capacity [12]. C_3H_6 is mainly used for the production of polypropylene, as well as for the synthesis of numerous platform chemicals (e.g., cumene, acrylonitrile, propylene-oxide) [13]. The importance of C_3H_6 in the C_3 value chain addresses the need for alternative processes; using the conventional technology, C_3H_6 can also be produced through C_4 - C_8 olefin cracking, or through FCC under severe conditions in order to increase produced volume [12]. On-purpose production methods that include propane dehydrogenation (PDH) [14], olefin metathesis [15], or methanol to olefins (MTO) [16,17], have recently been implemented, as well as using other unconventional feedstocks [18], such as bio-alcohols and vegetable oils.



Figure 3. C₃H₆ production methods using hydrocarbon feedstocks. Reproduced from [3]. 2014, WILEY-VCH Verlag GmbH & Co. (*XTP refers to propylene production from any kind of feedstock).

 C_4 olefins are mostly produced via fluid catalytic cracking, as well as through steam cracking (Figure 4). Most common C_4 olefins are C_4H_6 , isobutylene, and butenes; C_4H_6 is a key chemical, currently used for the production of polymers (i.e., rubbers), butylenes are expended in the fuel industry for the production of blending components and octane enhancers, and n-butenes are used as co-monomers of polyethylene and for the synthesis of higher olefins. C_4H_6 is the prevalent C_4 olefin, conventionally co-produced via naphtha and gas oil cracking, along with C_3H_6 and C_2H_4 , among others; C_4H_6 yield via cracking is substantially low, highlighting the need for more targeted production methods [4]. Demand for C_4H_6 is expected to increase, as it can be used as a bio-based feedstock for greener rubbers. Several bio-based routes have based proposed for C_4H_6 - production; bio-ethanol constitutes the most promising feedstock for this purpose.



Figure 4. C₄ olefin production methods using hydrocarbon feedstocks. Reproduced from [3]. 2014, WILEY-VCH Verlag GmbH & Co.

Overall, existing olefin production is highly dependent on fossil resources that are expended into energy-consuming processes, heavily contributing to the environmental affliction. Continuously increasing demand has turned the petrochemical industry towards optimization of existing processes in order to meet challenging capacities, while lowering the vast production costs. Recently, investigation of alternative feedstocks has been considerably studied in order to offer an attractive solution untrammeled from the limited crude oil reserves; coal, natural gas, and biomass are some of the examples [2,4]. Coal has been used in coal-rich countries as a feedstock for chemicals' production; even though it reduces dependence on fossil resources, the resulting CO_2 emissions limit the extent of its applications [4]. Methane prices have recently dropped due to technological advances, enabling the use of shale gas as an attractive, economical feedstock. Thus, cost-effective olefin production, via steam cracking, has been enabled, already implemented in the olefin market, primarily for the production of C_3H_6 and higher olefins [12,19,20]. Renewable feedstocks offer great advantages in terms of sustainability, energy consumption, environmental pollution, CO_2 emissions, and cost; biomass is an abundant carbon-source with potential to replace fossil resources [21]. Through processes such as fermentation, hydro-deoxygenation or gasification, light olefins can be produced from bio-feedstocks, or from bio-intermediates (e.g., ethanol, butanol, naphtha, methanol, and propane) via dehydration, metathesis, and steam-cracking, among others [22].

In this context, the alternative production of olefins from biomass intermediates is reviewed and compared to the conventional processes, with emphasis on the most promising chemical technologies for future applications that progress biomass valorization.

2. Olefins from Biomass

Following the incessantly increasing demand worldwide, technological advances have enabled the production of light olefins from various biomass-derived feedstocks, obtaining mainly mixtures of C_2 - C_4 olefins. Specific processes can be selective to the production of a certain product, as will be discussed in this chapter. Overall, olefins from biomass are predominantly produced from biomass intermediates, and more specifically, from alcohols, diols, and other oxygenates. These intermediates are, in most cases, formed via fermentation, hydro-deoxygenation, or gasification processes (Figure 5).



Figure 5. Biomass to olefins primary routes.

2.1. Ethylene (C_2H_4)

As mentioned above, steam cracking (mainly using naphtha as a feedstock) is the most extensively used process for C_2H_4 production from hydrocarbons. Steam cracking operating conditions require vast amounts of energy, thus increasing the production cost, and heavily contributing to environmental issues. Even though the installed technology for these processes has already been modified for increased efficiency, novel production methods have been explored in order to reduce production cost and to substitute the finite fossil resources. Apart from C_2H_4 conventional production from petrochemicals, C_2H_4 can be effectively produced from renewable feedstocks, such as plants, microorganisms, and bio-alcohols (Figure 6).



Figure 6. Schematic chart of C₂H₄ production methods.

 C_2H_4 biosynthesis is a natural pathway, as it constitutes an important hormone that plants recognize and produce [11]. ACC synthase and oxidase are two vital enzymes that enable C_2H_4 production from ACC (1-aminocyclopropane-1carboxylic acid) and SAM (S-adenosyl methionine), along with carbon dioxide and HCN, via the Yang cycle, starting from methionine via three consecutive reaction steps: (a) methionine is converted into SAM by SAM synthetase; (b) ACC synthetase converts SAM to ACC; and finally, (c) ACC is converted into C_2H_4 by ACC oxidase [23]. (Scheme 1) Microorganisms, such as bacteria and fungi have also been reported to produce C_2H_4 starting from methionine via the KMBA (2-keto-4-methylthiobutyric acid) formation pathway or through 2-oxoglutarate conversion [24–26]. Ethylene production rate can reach 2859.2 µmol/gCDW/h (CDW-Cell Dry Weight) from *Pseudomonas putida* [27]. Despite the fact that bio-synthesis technology is at its early stages, recent techno-economic analyses highlight the potential of these processes for on-purpose C_2H_4 production. However, further studies are required in order to reduce cost and overcome or improve aspects such as productivity and product separation. Advances in the biotechnological processes could improve productivity and reduce cost, enabling future development of C_2H_4 biosynthesis methods [28].



Scheme 1. Steps for C₂H₄ bio-synthesis.

Ethanol, derived from biomass, i.e., cellulose, corn, and sugarcane [8] is the most common bio-feedstock for the production of C_2H_4 . Several companies worldwide, such as Braskem (Sao Paulo, Brazil), Axens (Rueil-Malmaison, France), Solvay (Brussels, Belgium), and BP (London, United Kingdom), focus on research and plant operation for ethanol dehydration into C_2H_4 [13–15], as the global demand for C_2H_4 is continuously increasing [29,30]. Even though each company has developed and installed specific technologies for this reaction, ethanol dehydration typically includes two steps; reaction of ethanol dehydration and purification of products [29]. Bio-ethanol can be produced via fermentation processes causing sugars to selectively break down into ethanol, at high rates, with limited by-product formation [31]. However, the strong dependence on sugar production costs limit their application [30,32]. More complex feedstocks with higher market availability and thus lower cost (i.e., cellulose, hemicellulose, and lignocellulose) are more attractive but their direct conversion into ethanol is challenging and has not been reported to be satisfactorily viable for applications in the industry [33].

Bio-ethanol dehydration is an endothermic reaction, requiring relatively moderate temperatures (i.e., 180–500 °C) and the presence of a catalyst. The mechanism of bio-ethanol dehydration consists of the following steps: (a) protonation of the hydroxyl group by an acid catalyst, (b) deprotonation of the methyl group by the conjugate base of the catalyst, and (c) rearrangement to form C_2H_4 (Scheme 2) [30]. The selection of the most suitable catalyst for bio-ethanol dehydration into C_2H_4 is of key importance, in order to lower reaction temperature and overcome common issues, such as catalyst deactivation due to coke formation, particle collision, and agglomeration [29,30]. Acid catalysts, such as zeolites and silicoaluminophosphates (SAPO), have been widely used for this reaction, over the last decades, as they promote selective conversion into the desired product, with extremely high conversion and selectivity values, despite the fact that catalysts need to be frequently regenerated [30,34]. Actually, SAPO catalysts are significantly active in this reaction, reaching 98.0% selectivity to ethylene, at 250 °C, over SAPO-11-4 and 98.4%, at 340 °C, over Mn-SAPO-34 [35,36]. However, over modified HZSM-5

and MCM-41 catalysts, selectivity to C_2H_4 is even higher (i.e., 99.0%) [37]. Moreover, alumina-based catalysts, such as Al₂O₃-MgO/SiO₂, exhibited high conversion and selectivity values (i.e., 99.0 and 97.0%, respectively) requiring regeneration over longer periods of operation [29]. Tungsten-based heteropolyacids, supported on various substances are highly selective at relatively low reaction temperatures (i.e., 180–250 °C) [38]. It has been proven that acid-base sites on the catalyst surface are linked with the product distribution of this reaction; ethanol dehydration most probably proceeds via the formation of intermediate species and highly depends on temperature, ethanol partial pressure, and the nature of acid-base sites [30,39–43]. In fact, as ethanol dehydration is an endothermic reaction, the reaction temperature strongly affects C_2H_4 yield. Basic catalysts, such as MgO or CaO have also been used with results that resembled those, over acidic catalysts. Phosphoric acid, oxides, molecular sieves, and other heteropoly acid catalysts can also be used for this purpose [29]. Syndol is a commercial catalyst, used by Halcon SD (USA), to obtain high ethanol conversion and selectivity to ethylene, at 400–500 °C [29,44–46]. Overall, a selection of the most promising catalysts for ethanol conversion into C_2H_4 are presented in Table 1.

$$CH_{3}-CH_{2}-O-H \longrightarrow CH_{3}-CH_{2}-O-H \xrightarrow{-H_{2}O} CH_{2}\xrightarrow{+}CH_{2} \xrightarrow{-HA} CH_{2}=CH_{2}$$

$$\overset{\frown}{\hookrightarrow} H-A \xrightarrow{\downarrow} A^{*} \overset{\downarrow}{\swarrow} \overset{\downarrow}{A^{*}}$$

Scheme 2. Mechanism of bio-ethanol dehydration to C₂H₄.

Catalyst	Ethanol Conversion (%)	Selectivity to C ₂ H ₄ (%)	Temperature (°C)	WHSV ^a /LHSV ^b (h ⁻¹)	Reference
Mn-SAPO-34	99.4	98.4	340	2.0 ^a	[35]
0.5%La-2%P-HZSM-5	100.0	99.9	240-280	2.0 ^a	[47]
TPA-MCM-41 *	98.0	99.9	300	2.9 ^a	[48]
SynDol **	99.0	96.8	450	26–234 ^b	[29,44-46]
STA-MCM-41 ***	99.0	99.9	250	2.9 ^a	[49]

Table 1. Selected catalysts for bio-ethanol dehydration to C₂H₄.

* tungstophosphoric acid (TPA), ** MgO-Al₂O₃/SiO₂, *** silicotungstic acid (STA). ^a Weight hourly space velocity (WHSV), ^b Liquid hourly space velocity (LHSV).

Methanol is another alcohol that can be converted into olefins, through the well-known methanol-to-olefins (MTO) process. The MTO reaction is one of the most important processes for producing olefins from a C_1 feedstock [50]. MTO was initially proposed, in 1977, by Mobil Corporation [51], followed by numerous research studies, focusing on the development of a commercially available technology [17,52]. Within this context, the first MTO plant was installed in 2010, in China, for the production of light olefins from coal [53].

Bio-methanol can be produced via several processes including pyrolysis, bio-synthesis, gasification, and electrolysis, using a wide range of biomass waste, such as agricultural, forest, and municipal [17,53–55]. Although most of these processes are currently under development, the installation of bio-methanol production units requires further studies on design and energy efficiency in order to ensure feasibility of large-scale application [56].

MTO is an autocatalytic reaction that conventionally takes place at moderate temperature (i.e., 300–450 °C), over acidic catalysts. A number of suggestions on the mechanism of MTO has been proposed, showing that most conclusions agree that the reaction network consists of at least three main pathways: (a) direct methanol conversion; (b) direct conversion of ethylene; and (c) ethane methylation by methanol [52]. Depending on the catalyst used, MTO can selectively yield mainly C_2H_4 and C_3H_6 ; most studies focus on methanol conversion into ethylene, as the main product. (Scheme 3)

Over SAPO catalysts and zeolites, bio-methanol can be selectively converted into light olefins; over SAPO-34, selectivity to C_2H_4 and C_3H_6 is 60.0%, at 350–425 °C [57]. Modification on the catalyst synthesis procedure strongly affects product distribution. Dimethyl ether-to-olefins (DMTO) is a similar process that yields the same products. Bio-dimethyl ether can be produced from lignocellulosic biomass, via pyrolysis and gasification, resulting in the formation of olefins (i.e., C_2H_4 and C_3H_6) and syngas, following the bioliq[®] concept developed in Karlsruhe Institute of Technology, which is already implemented in a large scale unit in Germany [58–60]. DMTO can take place at high temperature (i.e., 723 °C) and low pressure (i.e., 4 bar), fully converting dimethyl ether (DME) into C_2H_4 (45.0%), C_3H_6 (39.0%), butenes (8.0%), and other light gases [10]. DME to olefins conversion is driven by a substantially complex reaction mechanism based on methylation, oligomerization, and hydrocarbon formation and cracking reactions, over zeolite catalysts [61].



Scheme 3. Bio-methanol conversion into olefins (MTO).

An overall comparison of the main C_2H_4 production processes is shown in Table 2. Despite of the technological advances of the last decades, bio-ethylene production processes cannot replace those dependent on fossil resources. As bio-synthesis processes are a recent research subject, further studies on the reduction of the cost and on increasing the productivity are essential prior to considering their industrial application. Bio-ethanol dehydration is the most promising alternative for the production of "green" C_2H_4 , as numerous studies have focused on the selection of the most suitable catalyst, lowering the reaction temperature, while increasing the yield to C_2H_4 . As ethanol dehydration has already been implemented, the only set-back for industrial bio-ethanol dehydration to C_2H_4 is the production and availability of bio-ethanol. MTO and DMTO processes have also been extensively studied with encouraging results regarding their commercial applications. Likewise, bio-methanol and bio-DME production is also limited, lowering prospect productivity. However, future increases of the produced bio-feedstocks could eliminate this issue, achieving high yields, in cost-competitive processes, as steam-cracking units. Future studies should focus on cost reduction linked with the implementation of the bio-based methods.

Process	Steam Cracking	Bio-Synthesis	Bio-Ethanol Dehydration	МТО	DMTO
Feedstock	HC (Naphtha)	ACC/SAM	Bio-ethanol	Bio-methanol	Bio-DME
Operating Conditions	675–700 °C atmospheric pressure	Ambient, aerobic conditions	180–500 °C	300–500 °C, low pressure	675–750 °C, low pressure
Advantages	Already installed technology	Selective sustainable production	Commercial application	Close to commercial application	
Disadvantages	Energy intense, environmental concerns, finite resources	Increased cost, low productivity	Limited bio-ethanol supply	Limited production of bio-feedstocks	
Yield to C ₂ H ₄	31.3%	-	99.9%	41.5%	45.0%

Table 2. Comparison of C₂H₄ production processes.

2.2. Propylene (C_3H_6)

As the demand for C_3H_6 increases, research focuses on on-purpose production of C_3H_6 , based on biomass resources, aiming at substituting oil-based feedstocks, in more environmentally friendly processes. Corn, vegetable oils and other biomass products have been effectively used as feedstocks for the production of bio-propylene, via processes such as gasification, metathesis, dehydrogenation, fermentation, and cracking [22]. Conventionally, C_3H_6 is a by-product of C_2H_4 production via steam cracking of hydrocarbons and FCC of gas oil. (Figure 7) At high temperatures, various hydrocarbons (e.g., naphtha, ethane, and propane) are co-fed, under the most suitable operating conditions, to selectively yield C_3H_6 [62]. FCC, also uses hydrocarbons to produce C_3H_6 , at moderate pressure and high temperatures, over zeolites, such as, ZSM-5, often modified with metals to increase selectivity to C_3H_6 [63]. It is considered greener than steam cracking due to lower energy demand and decreased CO_2 emissions. Apart from the well-known steam cracking and FCC, olefin metathesis and methanol to C_3H_6 are also considered alternatives for industrial application. Moreover, alkanes can be converted into alkenes via catalytic dehydrogenation; propane can be used as a feedstock, at high temperature and atmospheric pressure. Propane dehydrogenation plants have already been installed worldwide by several companies; Linde/BASF (Alabama, USA), Lummus Technology (New Jersey, USA), Snamprogetti/Yarsintez (Jubail, Saudi Arabia), UOP (Illinois, USA), etc., mostly using chromium, and Pt–Sn catalysts [64]. Methanol to C_3H_6 is actually included in methanol to olefins reactions, described in the previous chapter; zeolites (i.e., ZSM-5) are the most active catalysts in order to selectively produce C_3H_6 from methanol [65].



Figure 7. Schematic chart of C₃H₆ production methods.

As mentioned above, bio-ethanol can be produced through various methods. Apart from constituting a valuable feedstock for C_2H_4 production, bio-ethanol can also be used for C_3H_6 production; C_2H_4 from bio-ethanol can undergo dimerization followed by the well-known metathesis reaction, along with butenes, thus producing C_3H_6 [66]. For this process, not only bio-ethylene can be derived from biomass (i.e., bio-ethanol), but also bio-butylene from bio-butanol dehydration [67]. In fact, butanol can be produced from bio-ethanol, via the Guerbet process, where higher alcohols can be formed, upon condensation of two primary alcohols [68]. For this purpose, basic oxides, such as MgO and hydrotalcites have been active in ethanol conversion into butanol, reaching 85% selectivity [69]. *N*-butanol can also be produced through fermentation; several companies (e.g., Versalis -San Donato Milanese, Italy, Global Bioenergies - Evry, France) have already developed biochemical processes for the production of C_4 alcohols. Through the ABE process (Acetone-Butanol-Ethanol), C_4 alcohols can be produced via carbohydrate fermentation by genetically modified micro-organisms [39].

The metathesis reaction can yield C_3H_6 using C_2H_4 and butenes as a feedstock, via two different approaches: (a) dimerization of bio-ethylene and then reaction with remaining bio-ethylene and (b) direct reaction of bio-ethylene and bio-butene. (Scheme 4) C_2H_4 dimerization processes have already been implemented in the industry (e.g., AlphaButol by Axens- Rueil-Malmaison, France), operating under relatively mild conditions (i.e., 0–100 °C) and over metal catalysts, such as Ti and Ni [70]. In direct reaction processes, (e.g., Olefin Conversion Technology-OCT ABB Lummus Global), both homogeneous and heterogeneous catalysts have been employed. Heterogeneous (e.g., tungsten, such as organometallic complexes. Tungsten oxides, supported on silica have been used for the OCT process, at temperatures above 260 °C and 30–35 bar, reaching more than 90.0% selectivity to C_3H_6 , for 60.0% butene conversion [71]. Pre-reduction treatment, as well as increased acidity obtained using more acidic supports, enhances catalytic activity at lower temperature [72]. Rhenium catalysts have exhibited selectivity ~100%, however fast deactivation requires continuous regeneration [73]. Molybdena catalysts have also been used in the Shell High Olefin Process (SHOP), producing α -olefins through the oligomerization of C_2H_4 , followed by olefin metathesis [74].

$$2 \operatorname{CH}_2 = \operatorname{CH}_2 \longrightarrow \operatorname{CH}_2 = \operatorname{CH}_2 - \operatorname{CH}_3 \longrightarrow \operatorname{CH}_3 - \operatorname{CH} = \operatorname{CH}_3 - \operatorname{CH}_3$$

$$CH_3 - CH = CH_{--}CH_3 + CH_2 = CH_2 \longrightarrow 2 CH_2 = CH_{--}CH_3$$

Scheme 4. C₃H₆ formation via metathesis.

Solely 1-butene, produced via bio-butanol dehydration, can also be used as a feedstock for C_3H_6 formation, as 1-butene is isomerized to 2-butene, and then both react via metathesis to form C_3H_6 and 2-pentene [75]. Moreover, oligomerization/cracking of C_2H_4 from bio-ethanol can result in C_3H_6 production [76–78]. The direct ethanol to C_3H_6 process (ETP) has recently been explored, over catalysts such as zeolites [79–81] and metal oxide catalysts [82–84] in order to increase yield to C_3H_6 against the most common by-products (i.e., C_2H_4 , butenes and aromatic hydrocarbons), improve stability and suppress coke formation. Thus, as the yield to C_3H_6 rarely exceeds 40.0%, the need for novel catalytic materials is imperative [85].

Other biomass-derived oxygenates, such as polyols, aldehydes, and ketones can also be converted into hydrocarbons through oxygen removal catalytic reactions (hydrogenation/ dehydrogenation, and hydro-deoxygenation). In this context, over transition metal oxides, glycerol and other C₃ oxygenated compounds can be converted into C₃H₆. Glycerol is a low cost molecule that can be produced via fermentation, transesterification and hydrogenolysis reactions, from biomass feedstocks. It can be upgraded into valuable compounds through a number of chemical or biological routes [33]. Glycerol to olefins (GTO) methods require the complete removal of oxygen, which is an intricate task. Its catalytic conversion into C₃H₆ is a novel research subject that has recently attracted attention; Hultenberg and Brandin recently filed a patent introducing the production of lower hydrocarbons (e.g., ethane, propane, and propene) from glycerol, over WO₃ on ZrO₂ and Pt on CeO₂ catalysts. [86] Fadigas et al. initially explored glycerol conversion, in a continuous flow process, over Ni, and Fe–Mo metal catalysts supported on activated carbon, obtaining high selectivity values to C₃H₆ [87]. Schmidt's group reported glycerol cracking into propanal, acrolein, C₃H₆, and C₂H₄, in three steps (i.e., dehydration, hydrogenation, and upgrading), over HZSM-5 zeolites, Pd/ α -Al₂O₃, and HBEA zeolites, respectively for each step/reaction [88].

Yu et al used Ir/ZrO_2 and H-ZSM5 catalysts, in two steps, in order to selectively produce C_3H_6 via hydro-deoxygenation in a fixed-dual-bed reactor. Over the optimized reaction conditions (i.e., 250 °C and 1 bar hydrogen pressure), selectivity to C_3H_6 reached 85.0%, for complete glycerol conversion [89]. (Table 3) Sun et al. used WO₃-Cu/Al₂O₃ catalysts, at 250 °C under hydrogen flow (atmospheric pressure) to obtain 47.4% selectivity to C_3H_6 for 100% glycerol conversion [91]. Combining WO₃-Cu/Al₂O₃ and SiO₂-Al₂O₃ in a dual-bed reactor, selectivity to C_3H_6 reached 84.8%. Mota et al, used Fe/Mo catalysts supported on activated carbon to obtain 100 glycerol conversion and 90.0% selectivity to C_3H_6 at 300 °C [92]. In all the above studies, a number of by-products has been detected in the gas phase (e.g., carbon dioxide, propane, and ethylene). Further studies by our group, in a batch reactor, over molybdena-based catalysts supported on carbon, report glycerol production

into C_3H_6 with 100% selectivity in the gas phase (88.0% glycerol conversion and 76.0% selectivity to C_3H_6) at 300 °C and under hydrogen atmosphere (80 bar) (Figure 8) [90]. Our group has also proven that reducible molybdenum oxides selectively drive this reaction into C_3H_6 , most probably via a reverse Mars—van Krevelen mechanism; formation of Mo⁴⁺ and Mo⁵⁺ species most likely drives the reaction to the formation of the desired product. C_3H_6 is most probably formed via two consecutive cycles, in a one-step reaction: (a) due to the presence of oxygen vacancies, the adsorption of glycerol proceeds with the two adjacent hydroxyls forming an unstable cyclic intermediate which in turn is released as 2-propenol and (b) the latter after re-adsorption with the remaining hydroxyl is further deoxygenated to C_3H_6 [93]. Dow Global Technologies have patented a GTO process in a batch reactor, reaching 96% selectivity to C_3H_6 for 24% glycerol conversion. Hydroiodic acid acts as a catalyst in subsequent reduction-oxidation cycles, over reductive atmosphere [92].

Catalyst	Glycerol Conversion (%)	Selectivity to C ₃ H ₆ (%)	Temperature (°C)	WHSV (h^{-1})	Reference
Ir/ZrO ₂ & HZSM-5-30	100.0	85.0	250	1.0	[89]
Fe–Mo/Black Carbon	88.0	76.0	300	-	[90]
WO ₃ -Cu/Al ₂ O ₃ & SiO ₂ -Al ₂ O ₃	100.0	84.8	250	-	[91]
Fe/Mo	100.0	90.0	300	5.4	[92]

Table 3. Selected catalysts for one-step glycerol conversion into C_3H_6 .



Figure 8. Effect of reaction time on selectivity over the Fe–Mo/BC_A catalyst (H₂ pressure: 8.0 MPa, temperature: 300 °C). Reproduced from [90]. Copyright 2015, Royal Society of Chemistry.

Bio-oil, produced from catalytic pyrolysis of fats, oils and other low-values compounds, can also be used as a feedstock for the production of olefins, through processes that are already used in the petrochemicals' industry [94]. Syntroleum Corporation has already implemented similar processed (i.e., Bio-Synfining), where vegetable oils and fats can be converted into fuels and propane [95]. Neste Oil is also using the NExBTL (Next Generation Biomass to Liquid) process in order to produce liquid fuels and olefins [96]. Through steam cracking and fluid catalytic cracking, liquid fuels and C_3H_6 can be formed, while via the first route olefins are primarily produced [97]. The first step of the steam cracking process is hydro-deoxygenation of fatty acids and triglycerides, resulting in green hydrocarbons and naphtha. Hydro-deoxygenation proceeds over conventional hydrotreating catalysts, under high hydrogen pressure and moderate temperatures (i.e., 280–400 °C) [98]. Noble metal catalysts have also been used, supported on carbon, silica, alumina, or zeolites [99]. The second step involves gasoline and C_3H_6 formation, while suppressing C_2H_4 and aromatics production. Table 4 summarizes the main characteristics of the most important C_3H_6 production methods. Through steam cracking C_3H_6 can be formed as a by-product of C_2H_4 production, at high temperatures, in a markedly energy intense process. Lower temperatures of FCC make this process more environmentally friendly, compared to steam cracking. However, yield to C_3H_6 is highly dependent on the feedstock and on the selected condition. Catalyst deactivation and product recovery are among the disadvantages of this rather popular method. Propane dehydrogenation is another C_3H_6 production process from finite resources that also requires high temperatures and atmospheric pressure. Recently installed units highlight the potential of this application for on-purpose C_3H_6 production at high yields. Via metathesis reactions olefins can be converted into C_3H_6 , at relatively low temperatures and moderate pressure. Bio-olefins are the most suitable feedstock but their availability limits the productivity of this method. Glycerol to olefins is a novel research subject that aims at the production of "green" C_3H_6 through catalytic reactions, at moderate temperature. Nonetheless, more in-depth research is essential on the most suitable catalysts that will selectively drive the reaction. Even though C_3H_6 production from glycerol is still a lab-scale application, future studies focusing on scale-up and techno-economic analyses will enable industrial application of these biomass-valorization processes.

Process	Steam Cracking	FCC	Dehydrogenation	Metathesis	GTO
Feedstock	HC	HC	Propane	Bio-olefins	Glycerol
Operating Conditions	750–900 °C, moderate pressure	500–550 °C, moderate pressure	500–700 °C, atmospheric pressure	0–260 °C, moderate pressure	250–400 °C, hydrogen pressure
Advantages	Already installed technology	Greener than Steam Cracking, Flexibility of operation	Already installed units	Already installed units	Sustainable production
Disadvantages	Energy intense, environmental concerns, finite resources	Yield depends on feedstock, catalyst deactivation, product recovery	Catalyst deactivation, endothermic reaction	Limited production of bio-feedstocks	Require hydrogen atmosphere, lab-scale
Yield to C ₃ H ₆	18.0%	25.0%	85.0%	90.0%	90.0%

2.3. Butadiene (C_4H_6)

Alternative feedstocks have been proposed in order to effectively produce bio-butadiene from renewable resources, thus substituting the energy consuming processes of naphtha cracking. In Figure 9, the various production processes for C_4H_6 are summarized.



Figure 9. Schematic chart of C₄H₆ production methods.

 C_4H_6 is also a by-product of C_2H_4 production through cracking of hydrocarbons. C_4H_6 production from bio-ethanol is a promising alternative that has been industrially implemented prior to the installation of naphtha cracking technologies; ethanol to C_4H_6 processes have been used since 1920, constituting the main production practice until the end of World War II [22,100]. Main routes of this process include dehydrogenation, dehydration, and condensation over suitable catalysts, either in one-step (i.e., Lebedev approach) (Scheme 5) or two-step processes (i.e., Ostromisslenski approach) (Scheme 6) [100]. In the first case, multifunctional catalysts have been employed, mainly alumina and magnesia-silica catalysts, via C_2H_4 dimerization and subsequent metathesis, while at the latter, ethanol was initially dehydrogenated into acetaldehyde, over copper-based catalysts, at moderate temperatures, and then ethanol reacted with acetaldehyde to form C_4H_6 , over Ta_2O_5 catalyst, as well as other oxides, supported on silica [101,102]. Several research projects suggest that aldol condensation of acetaldehyde is a key step in ethanol conversion into C_4H_6 [103]. On the other hand, latest works,

including DRIFTS (Diffuse Reflection Infrared Spectroscopy) analyses and DFT (Density Functional Theory) calculations, propose that ethanol carbanionic intermediates are of key importance for the reaction mechanism [104].

$$2 C_2 H_6 O \longrightarrow C_4 H_6 + 2 H_2 O + H_2$$

Scheme 5. C₄H₆ production through the Lebedev process.

1. $C_2H_6O \longrightarrow C_2H_4O + H_2$ 2. $C_2H_6O + C_2H_4O \longrightarrow C_4H_6 + 2H_2O$

Scheme 6. C₄H₆ production through the Ostromisslenski process.

Apart from bio-ethanol, C_4H_6 can be formed from other biomass derived oxygenates such as butanols and butanediols, produced through biomass fermentation or gasification [105,106]. In fact, bio-1,4-butanediol is currently produced by Genomatica, at a small scale plant, planning on installing an industrial scale one with Novamont [107]. Acid catalyzed dehydration of bio-butanols yields a mixture of n-butenes. Subsequent dehydrogenation results in the production of C₄H₆. N-butanol can be converted into 1-butene or nonlinear C_4 olefins, via dehydration, over catalysts with mild or high acidity, respectively; over zeolites a ~60% yield to isobutene has been obtained [108]. The overwhelming cost of the butene dehydrogenation step has led to research on direct dehydration of butanediols to C₄H₆, over suitable catalysts; over sodium phosphate catalysts, 1,4-butanediol can be converted into C₄H₆ at 280 °C, while conversion of 1,3-butanediol requires higher temperatures, over the same catalysts [109]. C_4H_6 yield up to 95% has been reported from 1,4-butanediol [110] and 90% from 1,3-butanediol [103]. In both cases, increased by-product formation is a critical issue that further studies on catalytic approaches could address. Dehydration of other C_4 diols (e.g., 2,3-butanediol) is much more challenging, requiring multiple and more complex reaction steps [111]. 2,3-butanediol, produced via glucose fermentation, can be converted into C_4H_6 , over scandium oxide catalysts, at high temperatures (i.e., 411 °C), reaching 88% yield. Using two catalytic beds, with scandium oxide and alumina, selectivity to C_4H_6 was 94%, proving the feasibility of direct double bond dehydration of 2,3-butanediol [91]. Alternatively, two-step processes, using two different catalysts (e.g., silica or alumina-based) for subsequent dehydrations, have also been proposed, yielding C_4H_6 via the formation of unsaturated alcohols [112]. Novel chemical and biochemical technologies enable the production of C₄H₆ from syngas originating from the gasification of biomass or waste gases from the steel industry; butanediols can be produced from syngas via fermentation [113]. As syngas can be produced from various organic materials, such as biomass, it is rather inexpensive. Thus, it is an excellent resource for the production of valuable bio-chemicals and bio-fuels [114]. Bio-catalytic

processes enable syngas fermentation in moderate conditions, increasing energy saving, improving product yield and involving less toxic compounds or products [115,116]. Despite the fact that syngas fermentation is still an immature approach, its future potential cannot be ignored.

As lighter olefins are most preferably produced via steam cracking, C_4H_6 production is rather limited through this process. Via dehydrogenation, butane—or butenes via oxidative dehydrogenation, can be selectively converted into C_4H_6 but the high temperatures and catalyst deactivation are key disadvantages impeding commercialization. Bio-ethanol conversion into C_4H_6 is the most promising alternative; numerous studies have focused on the selection of the most suitable catalyst. However, catalytic deactivation and increased by-product formation are still critical issues that further research could resolve. Via dehydration/hydrogenation steps, bio-butanol can be effectively converted into C_4H_6 , but the limited availability of the feedstock, along with the significantly high cost due to high temperature (up to 700 °C) and to the hydrogenation step, hinder industrial application. (Table 5) On the other hand, relatively lower temperatures of highly selective bio-butanediol dehydration could enable its applicability, even though production of the bio-feedstock is quite limited and by-product formation is not negligible. To conclude, all bio-based methods for C_4H_6 production are still in lab-scale. Nonetheless, in the future, novel catalysts can be synthesized for the selective C_4H_6 production. Moreover, further studies on production of the biomass-derived feedstocks could reduce the cost and increase their availability in order to facilitate the implementation of these processes.

Process	Steam Cracking	Dehydrogenation	Lebedev/Ostromisslenski	Dehydration
Feedstock	Naphtha	Butane/Butenes	Bio-ethanol	Bio-butanediols
Operating Conditions	750–900 °C, moderate pressure	600–700/400–500 °C	400-650 °C	250–350 °C
Advantages	Installed technology	Well-established technology, on-purpose production	Bio-based, on-purpose production	Bio-based, on-purpose production
Disadvantages	Energy demanding, environmental concerns, finite resources, limited production	High endothermicity, catalyst deactivation	Catalyst deactivation, various by-products	Limited production of bio-feedstock, various by-products
Yield to C ₄ H ₆	4.5%	70.0%/71.8%	72.0%/56.5%	up to 95.0%

Table 5. Comparison of C₄H₆ production processes.

3. Concluding Remarks

Production of bio-olefins is a broad research field that is continuously expanding, as the demand is incessantly increasing, worldwide. Biomass derived intermediates offer numerous opportunities for alternative reaction pathways, yielding ethylene, propylene, or butadiene, in less energy demanding and cost effective processes that do not exploit the finite fossil resources. Bio-olefins can be produced via numerous processes, some of which have already been implemented in industrial applications.

Ethanol dehydration is the most promising bio-based process for bio-ethylene production that has already been installed, operating at relatively moderate temperatures. MTO and DMTO are close to commercial application, using bio-methanol and bio-DME as feedstocks, for selective ethylene production. In all cases, limited bio-ethanol supply is a key drawback that affects possibility of industrial applications. Bio-synthesis is an interesting research subject on selective sustainable production, but more in-depth studies are essential in order to increase productivity and significantly lower the cost.

Bio-propylene can be effectively produced through bio-olefin metathesis and glycerol to olefins methods, operating at relatively moderate conditions with increased bio-propylene yields. In fact, olefin metathesis technology has already been implemented; however, limited bio-feedstock availability strongly affects productivity and viability of this process. GTO methods include a wide range of processes that could yield bio-propylene in lab-scale applications. Nevertheless, studies on the most efficient and stable catalyst that will lower hydrogen demand are expected to make these processes applicable in the near future.

Bio-butadiene can be primarily produced from bio-ethanol via the Lebedev/Ostromisslenski methods that have been extensively studied in the past decades. Dehydration of bio-butanediols is the most promising approach, reaching 95% yield to butadiene, at lower temperature than the other alternatives. Bio-butanol can also be used as a feedstock for bio-butadiene production, but the high operation cost due to hydrogenation step and high temperature limits feasibility of implementation. Additionally, C_4 bio-feedstock production is also limited in order to ensure future viable industrial applications.

Overall, several bio-based processes have been proposed with high potential in bio-olefin yields. Even though the majority of them are still in laboratory scale, a few have already been implemented around the world. The main drawback in the scale-up of these processes is the availability of the bio-feedstocks which can be produced from various biomass derivatives via fermentation, bio-synthesis, cracking, and deoxygenation among others. Future studies should mainly focus on increasing the productivity of these methods, along with reducing the cost, in order to facilitate their implementation in bio-olefin production units. In most catalytic approaches, novel low-cost catalytic systems with improved properties regarding selectivity and reaction conditions should also be researched to advance future applications.

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